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20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

This TOP prescribes a method for evaluation of missile system materials and identifies chemical analysis tests, facilities, and equipment for use, as appropriate. It provides procedures for propellant, gas, and metal tests. Applicable to missile system material properties determinable by chemical tests.

US ARMY TEST AND EVALUATION COMMAND
TEST OPERATIONS PROCEDURE

DRSTE-RP-702-104 11 December 1975
Test Operations Procedure 5-2-585*
AD No.

CHEMICAL TESTS: PROPELLANTS, GASES, AND METALS

The use of trade names in this test operations procedure does not constitute an official endorsement or approval of the use of such commercial hardware or software. This test operations procedure may not be cited for purposes of advertisement.

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*This TOP supersedes TOP 5-2-585, 15 February 1972

1. SCOPE

a. This TOP establishes chemical analysis test procedures for evaluation of missile system material properties. The procedures provided are applicable to missile propellants, gases, and metals. Material properties are determined to insure conformance with project requirements. The tests used to measure these properties are derived from military specifications or conventional methods, or are developed specifically to meet a new requirement.

b. The following test procedures have been omitted from this TOP, since they are available in the military specifications listed below and would only serve as duplications here:

(1) Analysis of aniline using perchloric acid titration — MIL-A-10450C

(2) Analysis of UDMH by gas liquid chromatography — MIL-P-25604D

(3) Determination of NO_2 in IRFNA — MIL-P-7254F

(4) Determination of total acidity in IRFNA — MIL-P-7254E (not conducted under MIL-P-7254F)

(5) Determination of HF in IRFNA — MIL-P-7254F

(6) Determination of HNO_3 in IRFNA — MIL-P-7254F

(7) Determination of water in IRFNA — MIL-P-7254F

(8) Determination of total solids in IRFNA — MIL-P-7254F

2. FACILITIES AND INSTRUMENTATION.

The equipment required for a specific test is listed in the procedure for that test.

2.1 Facilities — A laboratory with the following equipment:

a. Laboratory glassware

b. Laboratory balances, 0-2000 gm ± 0.1 gm

c. Analytical balances, 0-200 gm ± 0.1 gm

d. Microanalytical balance, 0-20 gm ± 0.0001 mg

e. Heating mantles

f. Hotplates

g. Drying oven

h. Vacuum oven

i. Electric oven, 1500°C

j. Refrigerator

k. Specific ion electrodes

l. pH meters

m. Potentiometric recorders

n. Darkroom facilities

2.2 Instrumentation

a. Gas chromatographs

b. Ultraviolet spectrophotometer

c. Infrared spectrophotometer

d. Atomic absorption spectrophotometer

e. Emission spectrograph

f. Neutron activation analysis system

g. X-ray diffraction diffractometer unit

h. X-ray vacuum spectrograph

i. Recording polarograph

3. PREPARATION FOR TEST. Operators will take the following action prior to conduct of a test:

a. Be familiar with test procedure

b. Be familiar with applicable safety directives

c. Inspect area for safety hazards

d. Insure that safety devices/equipment are in satisfactory condition and immediately available

e. Take from storage only those reagents and equipment needed for conduct of test

f. Have test procedure available

g. Have equipment operations manual available

h. Insure that equipment indications are normal prior to energizing

i. Correct safety hazards

j. Insure that instruments to be used have been calibrated as required

3.1 Safety Doctrine

3.1.1 Operating Practices: Safety practices will be followed as prescribed by applicable regulation. In addition, special emphasis is placed on the following points:

a. The individual operator is directly responsible for conducting each task in a safe and efficient manner.

b. The task leader is responsible for the coordination of concurrent tasks so that interfering activities do not occur.

c. The supervisor is responsible for the state of training, elimination of hazards, housekeeping, and the enforcement of safe practices and compliance with regulations.

3.1.2 Prevention of Hazards: Personnel will exercise due care and common sense in the performance of their duties. Prevention is the preferred means of dealing with hazardous conditions. Prevention of hazards will be accomplished by:

a. Prior planning and organization

b. Evaluating each task for the hazards involved

c. Correcting hazards before proceeding

d. Maintaining an alert and vigilant attitude at all times.

e. Proper and continuous housekeeping. Storage areas will be kept free of clutter and excess supplies.

f. Storing and handling reagents and test samples with full regard for their dangerous properties and compatibility limitations. Materials which are respiratory hazards will be handled inside the fume hoods only.

g. Maintaining equipment in a safe working condition. The use of unsafe equipment is prohibited.

3.1.3 Correction of Hazardous Conditions: Chemistry laboratory personnel will take the following steps to correct hazardous conditions:

a. Stop operations in any area in which hazardous conditions exist

b. Immediately bring deficiency to the attention of the operator responsible

c. Take necessary corrective action

d. Notify supervisor of incident and action taken

3.1.4 Safety Consciousness: Personnel will be completely familiar with applicable procedures before undertaking an unfamiliar task. Routine operations will be performed in an alert manner. Safety consciousness will be stressed at all times in all operations.

3.1.5 Improved Operations: Personnel will maintain high safety standards and will strive to incorporate new procedures to make operations safer.

3.1.6 Safety Training and Related Requirements: Training of personnel will include the following considerations:

a. Each person working with toxic, flammable, or explosive chemicals will be instructed in the hazards relating to the handling of these chemicals.

b. Supervisory personnel will assure that no person will work with hazardous chemicals without being informed of associated hazards.

c. Supervisory personnel will provide each person working with hazardous chemicals with necessary protective equipment; e.g., fume hoods, glove boxes, gloves, aprons. fire extinguishers, emergency eye wash and shower facilities, etc.

d. A standing operating procedure (SOP) will be written for each hazardous operation or each group of hazardous operations before such operations commence.

3.2 Administrative Data - The following data should be recorded for each sample received for analysis:

a. Type of sample

b. Source

c. Project/project representative

d. Analytical support provided

e. Test results

f. Date received/date completed

4. TEST CONTROLS

4.1 General Procedure

a. Insure that safety devices and equipment are available and in use.

b. Keep aisles and passageways clear.

c. Insure that applicable procedure is being followed.

d. Insure that appropriate test equipment manual is being followed.

e. Monitor equipment for normal operations during test conduct.

f. Keep work area uncluttered.

g. Check test results for validity before reporting them. After test is conducted, perform the following actions:

(1) Place reagents and supplies in proper storage.

(2) Clean glassware and place it in storage.

(3) Dispose of toxic wastes in accordance with pertinent directives.

(4) De-energize equipment and inspect for normal indications.

(5) Correct safety hazards.

4.2 Evaluation of Test Results

a. Examine test results for accuracy before reporting them. In all cases, but particularly when test results fall outside the range normally encountered, review test steps to insure that test data is valid and not affected by procedural errors. When necessary, correct deficiencies and repeat tests. If discrepancies cannot be determined, conduct the test on a known sample.

b. Replicate results should fall within the limits given in the specific procedure.

c. Where limits are not given, the following values apply for routine procedures using normal care:

(1) Volumetric analysis: 2 parts per 1000

(2) Instrumentation analysis: 1%

(3) Emission spectroscopy: 10%

d. When desired precision is not attained, examine and correct, as necessary, operator technique and condition of equipment before repeating analysis for record.

5. TEST PERFORMANCE

5.1 Analysis of Hydrogen Peroxide by the Ceric Sulfate Method

5.1.1 Objective: Determine the strength of hydrogen peroxide solutions used as monopropellant pressurization agents in rocket systems

5.1.2 Standards: H_2O_2 in monopropellant pressurizing agents 90% + 1% - 0.5%, 70% + 1% - 0.5%; H_2O_2 in laboratory oxidizing agents 30% + 2% - 1%

5.1.3 Method

a. Scope. This method is primarily intended for highly concentrated (70 to 90 percent) solutions of hydrogen peroxide. Hydrogen peroxide solutions are extremely susceptible to decomposition through contamination; therefore, the use of specially passivated glassware is imperative. The analysis should be conducted promptly to minimize sample decomposition.

b. Equipment Required.

(1) Automatic zero burette, 50 ml

(2) Erlenmeyer flasks, 250, 500 ml

(3) Pipets, 1, 2, 5, 25 ml

(4) Bottle with eyedropper, 30 ml

(5) Volumetric flask, 1000 ml

(6) Weighing boat

(7) Single-pan analytical balance, 0-200 gm ± 0.1 mg

(8) Glass bottles, 9-liter

(9) Double-pan laboratory balance, 0-2000 gm ± 0.1 gm

(10) Brass weight set, 100 gm to 2000 gm

c. Preparation of Glassware. Wash glassware intended to hold H_2O_2 solution in a solution of synthetic detergent. Immerse the glassware in 10 percent NaOH solution for one hour, then rinse with tap water. Immerse the glassware in sulfuric acid solution, 35 percent by volume, for one hour at room temperature. Rinse the glassware in distilled water and dry in an oven at 105°C.

d. Preparation of Ceric Acid Sulfate Solution (0.1N). Weigh 300 gm of ceric sulfate ($Ce(SO_4)_2$). Transfer the ceric sulfate to a 9-liter bottle. Add distilled water until the bottle is half full. Slowly add 300 ml of sulfuric acid while continuously agitating the bottle. Fill the bottle to the 9-liter mark with distilled water. Stir thoroughly. Allow solution to settle. Filter solution before use.

e. Preparation of Ferrous Sulfate Solution (0.1N). Weigh 250 gm of ferrous sulfate heptahydrate ($FeSO_4 \cdot 7H_2O$). Transfer the ferrous sulfate to a 9-liter bottle. Add distilled water until the bottle is half full. Slowly add 100 ml of sulfuric acid while continually agitating the bottle. Fill the bottle to the 9-liter mark with distilled water and mix thoroughly.

f. Determination of the Ceric Acid Sulfate Equivalence Ratio.

(1) To each of three 250-ml flasks add 25.00 ml of 0.1N ceric acid sulfate (CAS) solution. Add to each flask four drops of ferroin indicator (commercially available). Titrate with 0.1N ferrous sulfate solution to the appearance of the orange red ferroin color. Record the volume of titrant used.

(2) Determine the CAS equivalence ratio (R) the same day the standardization or analysis is to be run, to correct for the effect of deterioration of Fe^{+2} solutions on contact with air.

g. Standardization of Ceric Acid Sulfate Solution.

(1) Prepare a 0.1000N potassium dichromate ($K_2Cr_2O_7$) solution by dissolving 4.9032 gm of $K_2Cr_2O_7$) with distilled water in a 1000-ml volumetric flask. Fill to the mark with distilled water. Mix thoroughly.

(2) Add 200 ml of distilled water to each of three 500-ml flasks. Pipet 25 ml of 0.1000N $K_2Cr_2O_7$ solution into each flask. Pipet 5 ml of sulfuric acid into each flask. Let stand for 5 minutes. Add to each flask 50.00 ml of 0.1N ferrous sulfate solution and stir continously. Add four drops of 0.025M ferroin indicator to each flask.

(3) Titrate each standard solution prepared in (2) above with the 0.1N CAS solution to the disappearance of the ferroin orange-red color. Record the volume of CAS solution to back titrate the excess $FeSO_4$ added to the $K_2Cr_2O_7$ solution.

h. Determination of the Strength of H_2O_2 Sample.

(1) Weigh a 100-ml volumetric flask to the nearest 0.0001 gm. Record the weight.

(2) Add 1 milliliter of hydrogen peroxide with a pipet. Weigh the flask to the nearest 0.0001 gm. Record the weight.

(3) Fill the flask to the mark with distilled water. Mix thoroughly.

(4) Add 50.00 ml of 0.1N CAS solution to each of three 250-ml flasks. Pipet into each 250-ml flask 5 ml of the hydrogen peroxide solution prepared in (3) above.

(5) To each flask add 4 drops of ferroin indicator. Titrate with 0.1N ferrous sulfate solution to the appearance of the orange-red endpoint. Record the volume of titrant used.

5.1.4 Data Required: Weight in grams to nearest 0.0001 gm; volume in milliliters to nearest 0.01 ml

a. To determine the CAS equivalence ratio (R):

(1) Volume of CAS solution

(2) Volume of $FeSO_4$ solution

b. To determine the normality of the CAS solution:

(1) Normality of $K_2Cr_2O_7$ solution (4 decimal places)

(2) Volume of $K_2Cr_2O_7$ solution

(3) Volume of $FeSO_4$ solution added to $K_2Cr_2O_7$ solution

(4) Volume of CAS solution to back titrate excess $FeSO_4$ solution added to $K_2Cr_2O_7$ solution

(5) The CAS equivalence ratio to 4 decimal places

c. To determine the strength of the H_2O_2 sample:

(1) Weight of empty 100-ml volumetric flask

(2) Weight of 100-ml volumetric flask plus sample of H_2O_2

(3) Weight of H_2O_2 sample

(4) Volume in H_2O_2 sample solution

(5) Volume in H_2O_2 aliquot used in the determination

(6) Volume of CAS solution to which H_2O_2 aliquot is added

(7) Volume of $FeSO_4$ solution used to back titrate excess CAS solution

(8) The CAS equivalence ratio

5.1.5 Data Reduction and Presentation

a. Determine the CAS equivalence ratio. Use the formula:

$$R = A/B \qquad (1)$$

where R = the CAS equivalence ratio

A = volume of CAS solution in milliliters

B = volume of $FeSO_4$ solution in milliliters

Take the average of the three values determined.

b. Determine the normality of the CAS solution. Use the formula

$$N = \frac{C \times D}{E \times R - F} \qquad (2)$$

where N = normality of the CAS solution

C = normality of the $K_2Cr_2O_7$ solution

D = volume of the $K_2Cr_2O_7$ solution

E = volume of the $FeSO_4$ solution added to $K_2Cr_2O_7$ solution

R = CAS equivalence ratio

F = volume of CAS solution to back titrate excess $FeSO_4$ added to $K_2Cr_2O_7$ solution

Take the average of the three values determined.

c. Determine the percent strength of the H_2O_2. Use the formula:

$$\% H_2O_2 = \frac{(G - H \times R) K \times 100}{W \times L/M} \quad (3)$$

where $\% H_2O_2$ = weight percent H_2O_2 content of the sample

G = volume of CAS solution to which H_2O_2 is added

H = volume of $FeSO_4$ solution to back titrate excess CAS solution

K = normality of CAS solution (N) × 0.01701 gm/meq (the milliequivalent weight of H_2O_2)

W = the weight of the H_2O_2 sample. (Item 5.1.4c(3)) Subtract the weight of the empty 100-ml volumetric flask from the weight of the 100-ml volumetric flask plus sample of H_2O_2.

L = volume of the H_2O_2 sample aliquot

M = volume of the H_2O_2 sample volumetric flask

Take the average of three determinations. The three results should agree within 0.5 percent.

5.2 Determination of Tin in Hydrogen Peroxide by Atomic Absorption Spectroscopy

5.2.1 Objective. Determine the tin content of hydrogen peroxide solutions. Tin compounds are used to stabilize solutions of concentrated hydrogen peroxide used as monopropellant pressurization agents in rocket systems.

5.2.2 Standards: For reagent grade H_2O_2, maximum Sn content is 1 part per million

5.2.3 Method

a. Scope. This method may be used to measure tin present in the parts-per-million range in hydrogen peroxide.

b. Equipment Required.

(1) Atomic absorption spectrophotometer set for use with air-acetylene flame

(2) Tin hollow cathode tube

(3) Volumetric flasks, 50, 100, 1000 ml

(4) Pipets, 25, 10, 5, 2 ml

(5) Weighing boat

(6) Single-pan analytical balance, 0-200 gm ± 0.1 mg

(7) Hydrometers, specific gravity range 1.000 to 1.400

(8) Graduated cylinder, 100 ml

c. Preparation of Glassware. Use glassware that has been carefully cleaned, then rinsed thoroughly with double-distilled water before drying.

d. Preparation of Reagents

(1) Prepare a 1000-microgram/milliliter stock solution of Sn. Dissolve 2.2471 gm of sodium stannate ($Na_2Sn(OH)_6$) in a 1000-milliliter

volumetric flask and dilute to the mark with double-distilled water. Mix. Transfer and store in a polyethylene bottle.

(2) Prepare a 100-microgram/milliliter Sn solution. Pipet 10 ml of the 1000-microgram/milliliter Sn solution into a 100-ml volumetric flask and fill to the mark with double-distilled water.

e. Operation of Equipment. Refer to the instruction manual to insure that the proper sequence of operations is followed to prepare and adjust the instrument, measure sample absorption, and de-energize the equipment. Special items to check in the sequence are:

(1) Installation and adjustment of the proper source lamp

(2) Proper setting of control parameters

(3) Proper wavelength settings and adjustments

(4) Operation of exhaust hood

(5) Operation of burner in strict compliance with instruction manual

(6) Absorption of samples and standards measured as shown in instruction manual

(7) Flame extinguished by shutting off fuel supply first, then shutting off air supply

(8) Power switch off

f. Conduct of Test

(1) Measure a 500-ml sample of hydrogen peroxide into a 1000-ml beaker. Add 200 ml double-distilled water. Place the beaker inside a fume hood, add about 10 mg powdered silver, and cover with a watch glass. When evolution of gas bubbles ceases, place the beaker on a hot plate and take to near dryness. Wash down the sides of the beaker with double-distilled water and filter solution into a 50-ml volumetric flask. Dilute to the mark with double-distilled water.

(2) Transfer a 5-ml aliquot portion of the sample into each of three 10-ml volumetric flasks labeled A, B, C. To flask A add no standard Sn solution, to flask B add 1 ml of 100-microgram/milliliter Sn solution, to flask C add 2 ml of 100-microgram/milliliter Sn solution. Fill each of the three flasks to the mark with double-distilled water. Mix thoroughly.

(3) Measure the absorption for each solution with the spectrophotometer using an air-acetylene flame. Record the absorption measurements.

(4) Determine the density of the hydrogen peroxide sample at 25°C. Use a calibrated hydrometer and apply the hydrometer correction. Record the hydrometer readings.

5.2.4 Data Required

a. Original sample volume in milliliters

b. Volume of concentrated sample in milliliters

c. Volume of aliquot portions in milliliters

d. Amount in milliliters of standard Sn solution added to sample aliquot portions

e. Volume in milliliters of test solutions

f. Absorption measurements of test solutions

g. Hydrometer reading and correction

5.2.5 Data Reduction and Presentation: Plot absorbance vs concentration.

a. Convert absorption measurements to absorbance units. Use conversion tables in the instrument operation manual.

b. Use rectangular coordinate graph paper. Plot absorbance versus concentration due to standard addition. Extend the line obtained to zero absorbance.

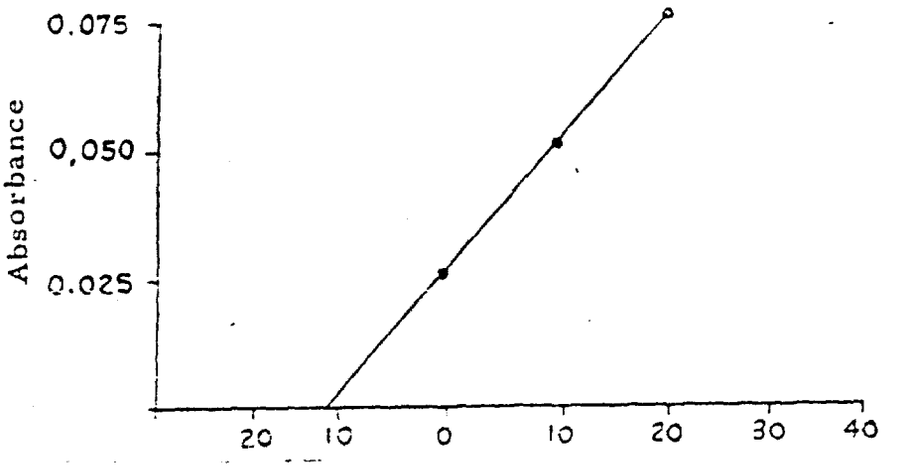

Fig. 1. Absorbance vs Concentration

The point of intercept on the zero absorbance axis is the Sn concentration of the test solution to which no standard additions were made.

c. Apply hydrometer correction to hydrometer reading. Use this value for the density in grams per milliliter.

d. Calculate the SN concentration of the original sample. Use the formula:

$$C = \frac{I \times \frac{V_4}{V_3} \times V_2}{V_1 \times D} \qquad (4)$$

where C = the Sn concentration of the original sample in parts per million by weight

I = the Sn concentration of the test solution with no additions in micrograms per milliliter

V_4 = volume in milliliters of test solution

V_3 = volume in milliliters of sample aliquot

V_2 = volume in milliliters of concentrated sample

V_1 = volume in milliliters of original sample

D = density of H_2O_2 sample in grams per milliliter

Sample Calculation:

$$C = \frac{10.3 \frac{\mu g}{ml} \times \frac{10\ ml}{5\ ml} \times 50\ ml}{500\ ml \times 1.1081 \frac{gm}{ml}} = 1.86 \frac{\mu g}{gm} = 1.9\ ppm$$

5.3 Potentiometric Determination of HCl in Rocket Exhaust Gas

5.3.1 Objective: Determine the HCl content of rocket motor exhaust gas samples to insure that proper protection against HCl respiratory hazard is provided launch personnel

5.3.2 Standards: Maximum five parts per million HCl in air

5.3.3 Method

a. Scope. HCl is present in the exhaust gases produced by the burning of solid propellants which contain chlorine-bearing compounds. This method is applicable for that portion of the chlorine content that has been converted to chloride ion (Cl^-). The Cl^- is determined with $AgNO_3$ using a potentiometric end point. The Cl^- is reported as HCl equivalent. The extreme sensitivity of this method requires that great care be taken to protect sample bottles, glassware, and reagents from contamination. The special construction of the sample bottles requires that they be handled and transported very carefully. The method does not cover sampling procedures, but it does prescribe preparation of gas sample bottles.

b. Equipment Required.

(1) Burette, 2 ml, graduated in 0.01 ml

(2) Pipets, 2 ml, 10 ml

(3) Volumetric flasks, 100 ml, 1000 ml, 2000 ml

(4) Beakers, 50 ml, 250 ml

(5) Water purity (conductivity) meter

(6) Volt/millivolt potentiometric recorder

(7) Silver electrode

(8) Calomel electrode

(9) Rubber hose

(10) H-cell

(11) Syringe, 5 ml

(12) Vacuum pump

(13) Barometer

(14) Mercury manometer, 1 meter

(15) Spherical gas bottles, 5 liter, with teflon stopcocks and O-ring seals

c. Preparation for Test.

(1) Prepare gas sample bottles. Use a water purity (conductivity) meter to determine the conductivity of the double-distilled water to be used in rinsing the sample bottles. Note the conductivity reading. Rinse each bottle at least three times with double-distilled water. Check the last rinse with the purity meter. When the conductivity of the rinse water is the same as the original value for the double-distilled water, the bottle is acceptable. Remove the water remaining in the gas bottle by rinsing with spectro grade acetone. Remove the acetone remaining by evacuation. After evacuation, check the bottle vacuum with the mercury manometer. Internal pressure in the bottle should be less than 5 mm Hg absolute. Check that the bottle valves are closed. Place the sample bottle in the transport container, making sure that the bottle fits smoothly, with no strain on the valves or stems.

(2) Prepare 1M KNO_3 solution. Dissolve 202.2 gm of analytical grade KNO_3 in a 2000-ml volumetric flask, using double-distilled water. Fill to the mark and mix.

(3) Prepare standard $AgNO_3$ solution 0.0100N. First, prepare a stock 0.1000N $AgNO_3$ solution by dissolving 16.989 gm $AgNO_3$ in a 1000-ml volumetric flask, using double-distilled water. Fill to the mark and mix thoroughly. Pipet 10 ml of the stock 0.1000N $AgNO_3$ solution into a 100-ml volumetric flask. Fill to the mark with double-distilled water and mix thoroughly.

(4) Prepare standard KCl solution 0.0100N. First, prepare a stock 0.1000N KCl solution by dissolving 7.455 gm analytical grade KCl in a 1000-ml volumetric flask using double-distilled water. Fill to the mark. Mix thoroughly. Pipet 10 ml of the stock 0.1000N KCl solution into a 100-ml volumetric flask, using double-distilled water. Fill to the mark. Mix thoroughly.

(5) Prepare H-cell. Rinse a clean H-cell with double-distilled water. Add 1 gram of agar to 25 ml of 1M KNO_3 solution. Heat to near boiling. When fluid, fill a 5-ml syringe. Hold the H-cell so that the crossbar is vertical and use the syringe to fill the crossbar. When the agar salt bridge has cooled, the cell is ready for use.

(6) Prepare silver electrodes. Clean the metallic tips of a pair of silver electrodes with detergent and scouring powder. Scour vigorously as required to prepare a clean surface. Rinse the tips in distilled water and immerse in saturated KCl solution. Connect one electrode to the positive pole of a 1.5-volt dry cell and the other electrode to the negative pole. Reverse current polarity to alternately clean and recoat the receptor electrode. When adequately coated, the receptor electrode will turn violet in color. Disconnect the electrodes and rinse the tips in distilled water.

(7) Prepare an electrode calibration solution by dissolving 12.82 gm of bromide-free KCl in 100 ml of distilled water.

(8) Check the coated electrode. Place about 50 ml of electrode calibration solution in a 100-ml beaker. Place a calomel electrode and the coated electrode in a suitable holder and immerse them in the calibration solution. Measure the potential. It should be between -18 mv and -25 mv at 20° to 30°C. Values outside this range indicate unsatisfactory silver electrode coating.

(9) Determine the chloride-free potential (endpoint). Rinse the electrodes with distilled water and install them in the H-cell. Place the coated silver electrode (Ag/AgCl) in the sample (drain) side of the H-cell. Place the calomel electrode in the reference side of the H-cell. Add 25 ml of 1M KNO_3 to each side. Connect the electrodes to a potentiometric recorder. With chloride-ion-free electrolyte in the Ag/AgCl halfcell, a potential of -265 mv to -270 mv will be measured.

NOTE: THE Ag/AgCl HALFCELL POTENTIAL MAY TEND TO SHIFT DUE TO THE CONDITIONS TO WHICH THE ELECTRODE HAS BEEN EXPOSED. FOR THIS REASON, DETERMINE THE CHLORIDE-FREE ENDPOINT BEFORE AND AFTER EACH DETERMINATION. TAKE THE AVERAGE OF THESE VALUES AS THE ENDPOINT. HIGH CONCENTRATION OF THE SILVER OR CHLORIDE IONS WILL TEND TO "SHOCK" THE Ag/AgCl ELECTRODE. AFTER SUCH EXPOSURE, ALLOW THE ELECTRODE TO REST IN 1M KNO_3 ELECTROLYTE FOR ABOUT 15 MINUTES, TO RECOVER ITS STABLE POTENTIAL. IF RECOVERY DOES NOT OCCUR, REPEAT PROCEDURES (6) THROUGH (9) ABOVE.

(10) Standardize $AgNO_3$ solution. Agitate the sample side of the H-cell by introducing a gentle, uniform flow of air through the gas inlet stem. Determine the chloride-free potential. To the sample side add 2 ml of standard 0.0100N KCl solution. Allow the system to come to a stable potential. Add standard 0.0100N $AgNO_3$ solution in increments. Allow the system to come to a stable potential between incremental additions. Record the $AgNO_3$ volumes on the voltage chart. Titrate 5 mv past the original chloride-free potential. Drain the sample side of the H-cell and refill with 1M KNO_3 solution. Determine the chloride-free potential. Average the before and after chloride-free potentials and use this value as the endpoint. Record the titrant volume that corresponds to this average endpoint value.

d. Determination of HCl in Field Samples.

(1) When the sample bottle is brought in from the field, inspect it closely for damage before removing it from the transport container. Carefully remove the gas sample bottle from the transport container. Connect the bottle to the mercury manometer. Open the stopcock of the bottle. Record the pressure. Close the stopcock and disconnect the bottle from the manometer. Record the barometric pressure.

(2) Clean a 50-ml beaker to insure its being Cl^- free.

(3) Add about 8 ml of 1M KNO_3 solution to the sample bottle. Close the stopcock and rotate the bottle so that the KNO_3 solution contacts all the interior surfaces of the bottle and thus extracts the HCl. Drain into the 50-ml beaker. Repeat the procedure until three extracts have been drained into the beaker.

NOTE: SET THE SAMPLE BOTTLE ASIDE FOR SPECIAL CLEANING AS DESCRIBED IN c(1) ABOVE.

(4) Determine the chloride-free potential of the H-cell. Drain the sample side and refill with the 25-ml KNO_3 extract. Titrate with standard 0.0100N $AgNO_3$ solution. Use procedure described in c(10) above. After titration, drain and refill the sample side of the H-cell with 1M KNO_3 solution and determine the chloride-free potential. Again use the average of the before and after chloride-free values as the endpoint. Record the titrant volume that corresponds to this average endpoint value.

5.3.4 Data Required

a. Barometric pressure to nearest millimeter Hg

b. Manometer pressure to nearest millimeter Hg

c. Volumes of $AgNO_3$ solution to nearest 0.001 ml

d. Volume of KCl standard solution to nearest 0.01 ml

e. Normality of standard KCl solution to three significant figures

f. Voltage recordings

g. Room temperature in degrees centigrade

h. Volume of sample bottle in liters to nearest 0.1 liter

5.3.5 Data Reduction and Presentation

a. Calculate normality. Use the formula:

$$N(AgNO_3) = \frac{\text{ml KCl} \times [N(KCl)]}{\text{ml } AgNO_3} \qquad (5)$$

Where $N(AgNO_3)$ = normality of standard $AgNO_3$ solution in milliequivalents per milliliter

ml KCl = volume in milliliters of 0.0100N KCl standard solution

N(KCl) = normality of standard KCl in milliequivalents per milliliter

ml $(AgNO_3)$ = volume in milliliters of standard $AgNO_3$ solution

b. Calculate the concentration of HCl in gas sample bottle in parts per million (ppm) by volume in air. Use the formula:

$$\text{ppm HCl} = \frac{A \cdot N(AgNO_3) \times 22.4 \times 10^6 \frac{\mu l}{mol} \cdot \frac{1 \text{ mol HCl}}{10^3 \text{ meq HCl}}}{V_s \left(\frac{P(INT)}{760 \text{ mm Hg}}\right)\left(\frac{273^\circ K}{Tr^\circ K}\right)} \quad (6)$$

Where ppm HCl = concentration of HCl in ppm by volume in air

A = volume in milliliters of standard $AgNO_3$ solution to titrate KNO_3 extract of sample bottle

$N(AgNO_3)$ = normality of standard $AgNO_3$ in milliequivalent per milliliter

V_s = volume of sample bottle in liters

$P(INT)$ = absolute pressure inside the sample bottle with sample collected in millimeters Hg. Determine P(INT) by subtracting differential manometer pressure from barometric pressure

Tr = room temperature in degrees K. Add 273 to room temperature in degrees centigrade.

Sample Calculation:

$$\text{ppm HCl} = \frac{0.052 \text{ ml} \times 0.0101 \frac{\text{meq}}{\text{ml}} \times 22.4 \times 10^6 \frac{\mu l}{mol} \times \frac{1 \text{ mol HCl}}{10^3 \text{ meq HCl}}}{5.0 \text{ lt} \times \frac{430 \text{ mm Hg}}{760 \text{ mm Hg}} \times \frac{273^\circ K}{296^\circ K}}$$

$$\text{ppm HCl} = 4.5 \frac{\mu l}{lt} = 4.5 \text{ ppm}$$

5.4 Determination of Dioctyl Adipate in Solid Propellant Using Infrared Spectroscopy

5.4.1 Objective: Determine the dioctyl adipate (DOA) content in solid propellant. Quantitative analysis of solid propellants is used either to confirm propellant identification or to determine extent of propellant deterioration.

5.4.2 Standards: Per applicable propellant specifications, which are classified. This method may be used as an alternate to Method T208.4, MIL-STD-286B.

5.4.3 Method

a. Scope. The infrared absorption spectrum of the sample is compared to that of a standard composition. The use of an internal standard makes it unnecessary to determine sample thickness. However, the internal standard mixture must have uniform composition.

b. Equipment Required.

(1) Dual-beam infrared spectrophotometer

(2) KBr pellet die

(3) Hydraulic press, 20 ton/in^2 capacity

(4) Microgram balance, 0-20 gm ± 0.000001 gm

(5) Single-pan analytical balance, 0-200 gm ± 0.0001 gm

(6) Stainless steel sample vials ("Wig-L-Bug")

(7) Sample vial shaker

(8) Vacuum pump with hose

c. Conduct of Test.

(1) Determination of Spectra (Instrument Parameters). Energize the spectrophotometer. Install chart paper and set wavelength to 4.0 microns. Set scale expansion at 1X. Adjust zero and 100 percent transmittance readings of the pen to the corresponding chart value. Set manual slit width to 75 microns. Place the pellet, containing the material under test, in the pellet holder. Insert the holder in the sample beam. Adjust the transmittance to 85 percent. Scan and record to 5.5 microns. (NaN_3 peak occurs at 4.75 microns.)

NOTE: IF THE NaN_3 PEAK EXTENDS BELOW 20 PERCENT TRANSMITTANCE, MAKE A NEW PELLET USING LESS MATERIAL.

At 5.5-micron wavelength setting, adjust the manual slit width to 100 microns. Scan and record to the 6.1 microns. Label each spectrum. Remove the pellet holder from the sample beam and rotate the pellet 45° from its original position. Reinsert the holder in the sample beam. Loosen the scan drive and reset wavelength to 4.0 microns. Move chart to unused area. Tighten scan drive and repeat scan of NaN_3 and DOA peaks as above. Repeat the procedure until the pellet has been rotated a total of 180° (four times).

(2) Prepare pellet. Weigh on a microbalance a clean, dry sample vial ("Wig-L-Bug"). Record the weight. Add the first ingredient. Weigh on the microbalance. Record the weight. Add the second ingredient. Weigh on the microbalance. Record the weight. Add the grinding ball and cap to the vial. Place the vial on the shaker and grind for 2 minutes. To make a pellet from this mixture, place the body of the die on its base. Insert the small, lower ram into the die opening with the shiny surface up. Transfer approximately 300 mg of the prepared KBr mixture to the die opening. Insert the top plunger and, with a light rotary motion of the plunger, level the sample. Connect the die to the vacuum system and evacuate the die to a pressure of 2 mm Hg for about 2 minutes to remove lightly held water from the surface of the KBr and to remove the air from between the KBr particles. With the vacuum still connected, place the die with the top platen, if required, on top of the ram. Press for 4 minutes at 10 tons of total force. Disconnect the die from the vacuum line, relieve the pressure of the press, and remove the die. Invert the die and remove the base. Place the inverted die back in the press, and center the split ring on the die so the lower plunger will be visible when forced from the die. Now, with the press, force the plunger upward until the lower ram and pellet just clear the body of the die. Remove the die from the press and, with tweezers, place the pellet in the pellet holder. Insert the pellet holder in the instrument. Determine and record the spectrum of the pellet.

(3) Prepare potassium bromide/sodium azide mixture. Mix in a grinder to a uniform consistency 20 gm powdered KBr and 0.026 gm NaN_3. Prepare three pellets. Identify and weigh each pellet. Determine the absorbance for each pellet of the NaN_3 peak at 4.75 microns [(1) above]. Divide the absorbance of NaN_3 peak of each pellet by its weight. The ratios should agree within two significant figures. If not, prepare a new mixture.

(4) Prepare synthetic propellant. Use the following reagents: (MEK) methyl ethyl ketone (reagent grade), (KBr) potassium bromide (ACS grade), (NH_4ClO_4) ammonium perchlorate (ACS grade). Establish the composition of the propellant to be analyzed, from specifications or similar documents. Weigh as in (2) sufficient DOA, NH_4ClO_4 and KBr to the nearest 0.02 mg to make a 1-gram sample whose composition approximates the composition of the propellant to be analyzed. Together, these materials are referred to as synthetic propellant. Moisten mixture with MEK.

WARNING: USE THE FUME HOOD FOR OPERATIONS INVOLVING MEK. GRIND AND MIX UNTIL THE PROPELLANT IS UNIFORMLY MIXED. PLACE THE PROPELLANT IN A VACUUM DESSICATOR AND EVACUATE TO REMOVE ALL TRACES OF MEK.

(5) Prepare a reference propellant mixture. Follow procedure in (2). First add 0.005 gm of synthetic propellant (4) to sample vial. Add NaN_3/KBr mixture (3) to make one gram. Record weights. Add grinding ball and cap. Proceed as in (2).

(6) Prepare a sample propellant mixture. Follow the procedure in (2). First add 0.005 gm of powdered propellant to be analyzed. Add NaN_3/KBr mixture (3) to make one gram. Record weights. Add grinding ball and cap. Proceed as in (2).

5.4.4 Data Required: Weight in grams to nearest 0.000001 gm.

a. Synthetic Propellant.

(1) Weight of sample vial (tare 1)

(2) Weight of tare 1 plus DOA

(3) Weight of tare 1 plus DOA plus NH_4ClO_4

(4) Weight of tare 1 plus DOA plus NH_4ClO_4 plus KBr

b. Reference Propellant Mixture.

(1) Weight of sample vial (tare 2)

(2) Weight of tare 2 plus synthetic propellant

(3) Weight of tare 2 plus synthetic propellant plus KBr/NaN_3 mixture

c. Propellant Mixture.

(1) Weight of sample vial (tare 3)

(2) Weight of tare 3 plus propellant

(3) Weight of tare 3 plus propellant plus KBr/NaN_3

d. Retain all chart recordings.

5.4.5 Data Reduction and Presentation

a. Calculation of the DOA Content:

(1) Construct baselines for all of the recorded scans by drawing the best straight line through the minimum absorption points for each scan.

(2) Determine the absorbance value ($\log \frac{I\ base}{I\ sample}$) for each NaN_3 and DOA absorbance peaks.

(3) Divide the absorbance (A) value for the DOA peak by the A value for the NaN_3 peak for each scan.

$$\frac{A(DOA)}{A(NaN_3)} \qquad (9)$$

(4) Average the values of this ratio for the scans on the reference propellant mixture pellet and the sample propellant mixture pellet.

(5) Use the relationship:

$$\frac{\text{Concentration DOA in Synthetic Propellant}}{\text{Average } \frac{A(DOA)}{A(NaN_3)} \text{ Reference Propellant Mixture}} = \frac{\text{Concentration DOA in Propellant}}{\text{Average } \frac{A(DOA)}{A(NaN_3)} \text{ Propellant Mixture}} \qquad (10)$$

The weight fraction of DOA in the synthetic propellant is determined by dividing the weight of DOA in the amount of reference propellant mixture by the total weight used to prepare the pellets.

b. Sample Calculations.

(1) Synthetic propellant:

Tare 1 + DOA		10.160035 gm	
Tare 1		10.128926 gm	
	DOA	0.031109 gm	9.86%
Tare 1 + DOA + NH_4ClO_4		10.336129 gm	
Tare 1 + DOA		10.160035 gm	
	NH_4ClO_4	0.176094 gm	55.82%
Tare 1 + DOA + NH_4ClO_4 + KBr		10.444412 gm	
Tare 1 + DOA + NH_4ClO_4		10.336129 gm	
	KBr	0.108283 gm	34.32%

(2) Reference propellant mixture:

Tare 2 + synthetic propellant	8.207142 gm
Tare 2	8.202113 gm
Synthetic propellant	0.005029 gm
Tare 2 + synthetic propellant + KBr + NaN_3	9.202181 gm
Tare 2	8.202113 gm
Reference propellant mixture	1.000068 gm

(3) Weight percent DOA in reference propellant mixture:

$$\text{Wt \% DOA} = \frac{0.005029 \text{ gm} \times 0.0986 \times 100}{1.000068 \text{ gm}}$$

$$\text{Wt \% DOA} = 0.04958$$

(4) Propellant mixture:

Tare 3 + propellant		10.134896 gm
Tare 3		10.129932 gm
	Propellant	0.004964 gm
Tare 3 + propellant + KBr + NaN_3		11.129908 gm
Tare 3		10.129932 gm
	Propellant + KBr + NaN_3	0.999976 gm

(5) Absorption data:

	$A(DOA)/A(NaN_3)$
Propellant mixture pellet	0.20780
Reference propellant mixture pellet	0.19772

(6) Weight percent DOA in propellant mixture:

$$\frac{0.04958}{0.19772} = \frac{\text{Wt \% DOA in Propellant Mixture}}{0.20780}$$

$$\text{Wt \% of DOA in Propellant Mixture} = 0.05211\%$$

(7) Weight percent DOA in propellant:

$$\text{Wt \% DOA in Propellant} = \frac{0.0005211 \times 0.999976 \times 100}{0.004964}$$

$$\text{Wt \% DOA in Propellant} = 10.5\%$$

5.5 Quantitative Analysis of Alloying Elements in Steel Using Emission Spectroscopy

5.5.1 Objective: Determine the content of alloying elements in steel

5.5.2 Standards: Not applicable

5.5.3 Method

a. Scope. This procedure is applicable to steels containing alloying elements in the concentration ranges shown in Table 1.

TABLE 1

CONCENTRATION RANGE FOR ANALYSIS OF ALLOYING ELEMENTS IN STEELS

Element	Concentration Range (percent)
Boron (B)	0.002 - 0.01
Chromium (Cr)	0.3 - 1.1
	2.5 - 25.0 (Stainless Steel)
Manganese (Mn)	0.3 - 1.5
Molybdenum (Mo)	0.2 - 1.0
Nickel (Ni)	0.1-1.0; 0.5 - 5.0
Silicon (Si)	0.1 -0.3
	0.3 -1.2
Vanadium (V)	0.005 - 0.15

b. Equipment Required

(1) Dual-grating emission spectrograph

(2) Plate reading densitometer

(3) Darkroom facilities

(4) SA-I type spectrographic plates, 4 x 10 inches

c. Preparation of Equipment

(1) Set the following conditions on the grating control panel of the emission spectrograph instrument:

(a) Separation to 0

(b) Light for grating #1 to 100 percent and #2 to 0

(c) Separation of spectra to 6 mm

(d) Movement of plate to down and automatic

(e) Wavelength range for grating #1 to the value listed in Table 2 for the element being determined

(2) Set the spectrograph slit controls as follows:

(a) Slit width to 20 microns

(b) Place filter #2 (7%/100%/33% transmission) into position

(c) Slit height to 6.5 mm

(3) Set spectrograph excitation unit to the following conditions:

(a) Capacitance and inductance switches to "short"

(b) Selector switch to the type of excitation listed in Table 2 for the element being determined

(c) Rotate spark power to its counterclockwise limit

TABLE 2

INSTRUMENT PARAMETERS

Element	Standard	Wavelength Range (Analytical Lines)	Excitation Selector Switch	Prespark Timer	Total Timer	Discharges Per Cycle
B	*	2100-3100	Uni-arc	10	15	2
Cr (Low)	*	2300-3300	Spark	10	21	10
Cr (High)	*	2000-3000	Spark	10	15	10
Mn	*	2300-3300	Spark	10	21	10
Mo	*	2300-3300	Spark	10	18	10
Ni (Low & High)	*	2400-3400	Spark	10	30	10
Si (Low)	*	2300-3300	Spark	10	24	10
Si (high)	*	2300-3300	Spark	10	21	10
V	*	2300-3300	Spark	10	21	10

*For the analysis of a specific element, select two standards whose concentrations of the element being determined closely approximate the expected value of the sample. The standard values should bracket the sample value.

(d) Rotate arc power to position #10.

(e) Set the prespark and total timers to the values listed in Table 2 for the element being determined.

(4) Place a carbon electrode in each holder and turn on the air flow regulator so that a reading of 3 pounds is obtained.

(5) Start the spectrograph and turn the spark power clockwise until the number of discharges established for the element being determined listed in Table 2 is obtained on the oscilloscope.

(6) Stop the spectrograph.

(7) Set the plate position to 6 on the plate position scale.

(8) Insert a loaded film holder into the film holder rack.

(9) All samples and standards must have a flat surface. Polish the surface of each sample on a belt sander to insure that it is clean and flat.

d. Conduct of test

(1) Employ the excitation sequence shown in Table 3 for the analysis of up to six unknowns.

(2) Pull the plate holder back cover up until it has reached the upper limit of travel as indicated by a metallic "click" sound.

(3) Start the unit and allow it to run the programmed cycle.

(4) Place the appropriate spectrographic steel standard in the lower electrode clamp, and place a 3/16-inch outside diameter electrode point-down in the upper clamp.

(5) Start the unit and, during the prespark time, adjust the electrodes to the red lines on the burner housing.

NOTE: THIS ADJUSTS THE ELECTRODE GAP TO 3 MM. DO NOT CHANGE THE ADJUSTMENT DURING THE EXPOSURE.

(6) Repeat steps (4) and (5), using the unknown sample in place of the standard. Run no more than three unknowns in series.

TABLE 3

EXCITATION SEQUENCE FOR ANALYSIS OF UP TO SIX UNKNOWNS

Spectrum No.	Sample
*1	Carbon
2	Standard (High)
3	Standard (Low)
4	Unknown
5	Unknown
6	Standard (High)
7	Standard (Low)
8	Unknown
9	Unknown
10	Standard (High)

*Spectrum 1 is run as a check on the electrode purity.

(7) Repeat steps (4) and (5), using the standard.

(8) Repeat steps (4) through (7) to analyze up to nine unknowns.

(9) Upon completion of excitation, turn the master switch (excitation unit) off, turn the lamp on the burner housing off, and turn the air off.

(10) Push the plate holder back cover down until it is in a closed position.

(11) Remove the plate holder and take it to the darkroom.

(12) Develop the plate.

5.5.4 Data Required: Retain the developed plate.

5.5.5 Data Reduction and Presentation

a. Determine the transmittance reading (Tr) of the analytical lines listed in Table 4.

b. Determine the average transmittance reading for each line.

c. Calculate the Seidel function value to four decimal places for each transmittance reading. Use the formula:

$$S = \log \left(\frac{100}{Tr} - 1\right) \qquad (11)$$

where S = the Seidel function

Tr = the transmittance reading

d. Subtract algebraically the S value for each internal standard Fe line from each corresponding sample line. The difference is a logarithmic intensity ratio.

e. Take the average of the log intensity ratios for the known sample concentrations.

f. Use semilogarithmic paper to plot percent concentration vs log intensity ratio for the known standard values. Plot percent concentration on log scale and average log intensity ratios on linear scale.

TABLE 4

ANALYTICAL LINES

Element	Element Line	Internal Standard Line (Fe)
B	2496.78	2496.99
Cr (Low)	2822.37	2813.61
Cr (High)	2324.89	2357.01
Mn	2886.68	2906.42
Mo	2775.40	2770.51
Ni (Low)	3012.00	3011.48
Ni (High)	3012.00	3011.48
Si (Low)	2881.58	2874.17
Si (High)	2516.12	2509.12
V	3110.71	3116.59

g. Use the log intensity ratio of the sample to determine the graphical value for the concentration of the sample.

5.6 Collection of Rocket Exhaust Gas Samples by Cascabel Sampler

5.6.1 Objective: Collect rocket exhaust gas samples in a precise time sequence. Rocket exhaust gases contain combustion products harmful to personnel. Since the exhaust cloud is of relatively short duration, a reproducible method of capturing representative samples is essential.

5.6.2 Standards: Not applicable

5.6.3 Method

a. Scope. The cascabel device is an automatic sequential gas sampler and may be used wherever there is access for a 5/8-inch outside diameter sampling line. There must be 110v ac, 60-Hz power available. The sampler must be protected from the rocket blast. The samples must be collected within the timing cycle (75 sec). Manual operation of the starting switch incorporates human error.

b. Equipment Required. An automatic sequential gas sampler (Figures 2 and 3). Whenever power is supplied to the chassis board of the gas sampler, the blower motor will operate continuously. The manual trigger must be on for the timer to function. When the manual trigger is on, power is supplied through the normally closed contacts of the delay relay. This power operates the synchronous motor which drives the eight cams which open and shut the eight microswitches. Each cam operates one microswitch which energizes one solenoid valve. Each cam can be set to operate for 0 to 100 percent of cycle anywhere between 0 and 100% of cycle. Normally the cycle length is 75 seconds with the sampling time of 3 seconds per sample. Most of the samples are taken close to T = 0, where experience shows that the highest concentration of exhaust fumes exists. At the end of the preset time, the delay relay shuts off power to the timer. The timer will not start again until the manual trigger is turned off and then on again.

c. Sampler Preparation and Installation

(1) Survey anticipated launch area and prepare blast protection for sampler boxes within it.

(2) Coordinate as required and establish the starting time for sampler (such as T minus 15 seconds).

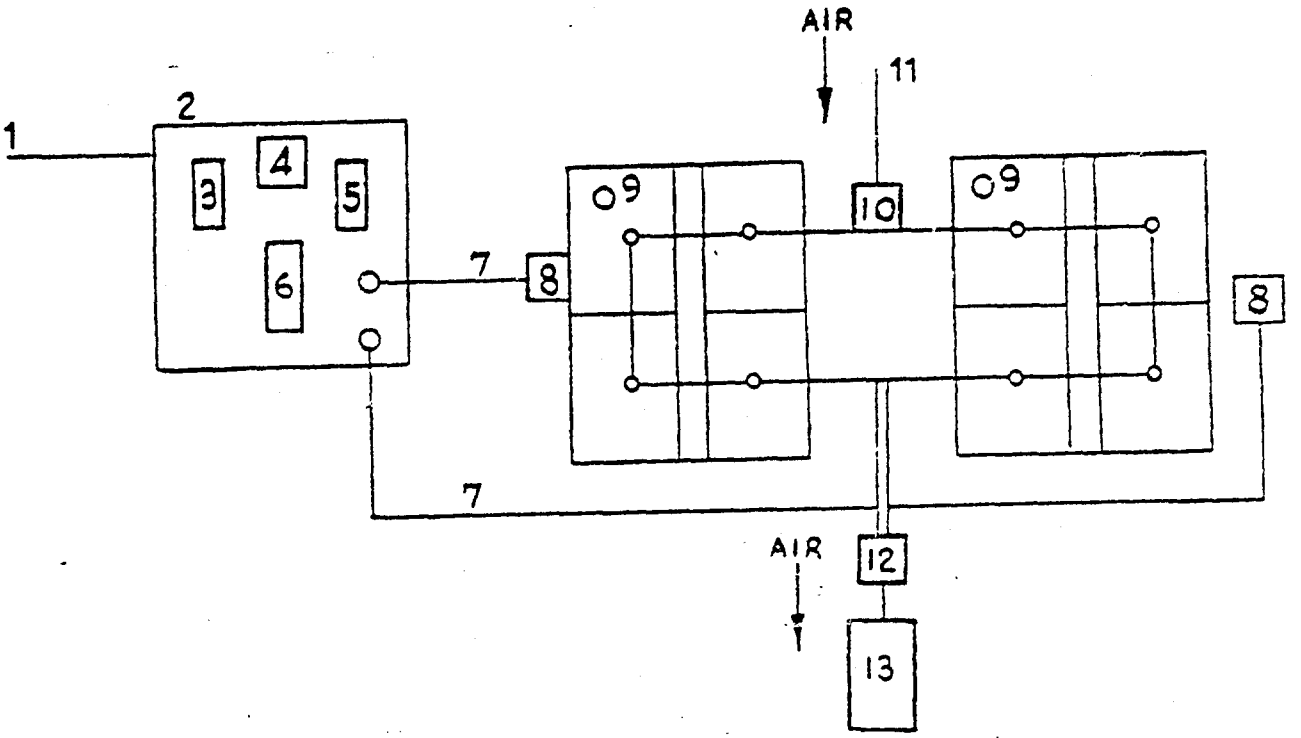

Fig. 2. Block Diagram of Sequential Gas Sampler

1. Three-conductor cord, 110v ac, 60 Hz, with cable reel, 250 ft
2. Chassis board (See Figure 3 for partial schematic.)
3. Power socket, blower socket
4. Delay relay, 0-180 sec
5. Trigger socket
6. Timer-synchronous motor with eight camdriven microswitches, one cycle 75 seconds
7. Jumper cables
8. Jumper plugs for four solenoid valves
9. Four-solenoid valve group with four (2-liter) vacuum flasks
10. Manifold system (one system per each four-solenoid valve group)
11. Polyvinyl chloride sampling line, 20 ft, 5/8-inch outside diameter
12. One-way check valve
13. Blower motor

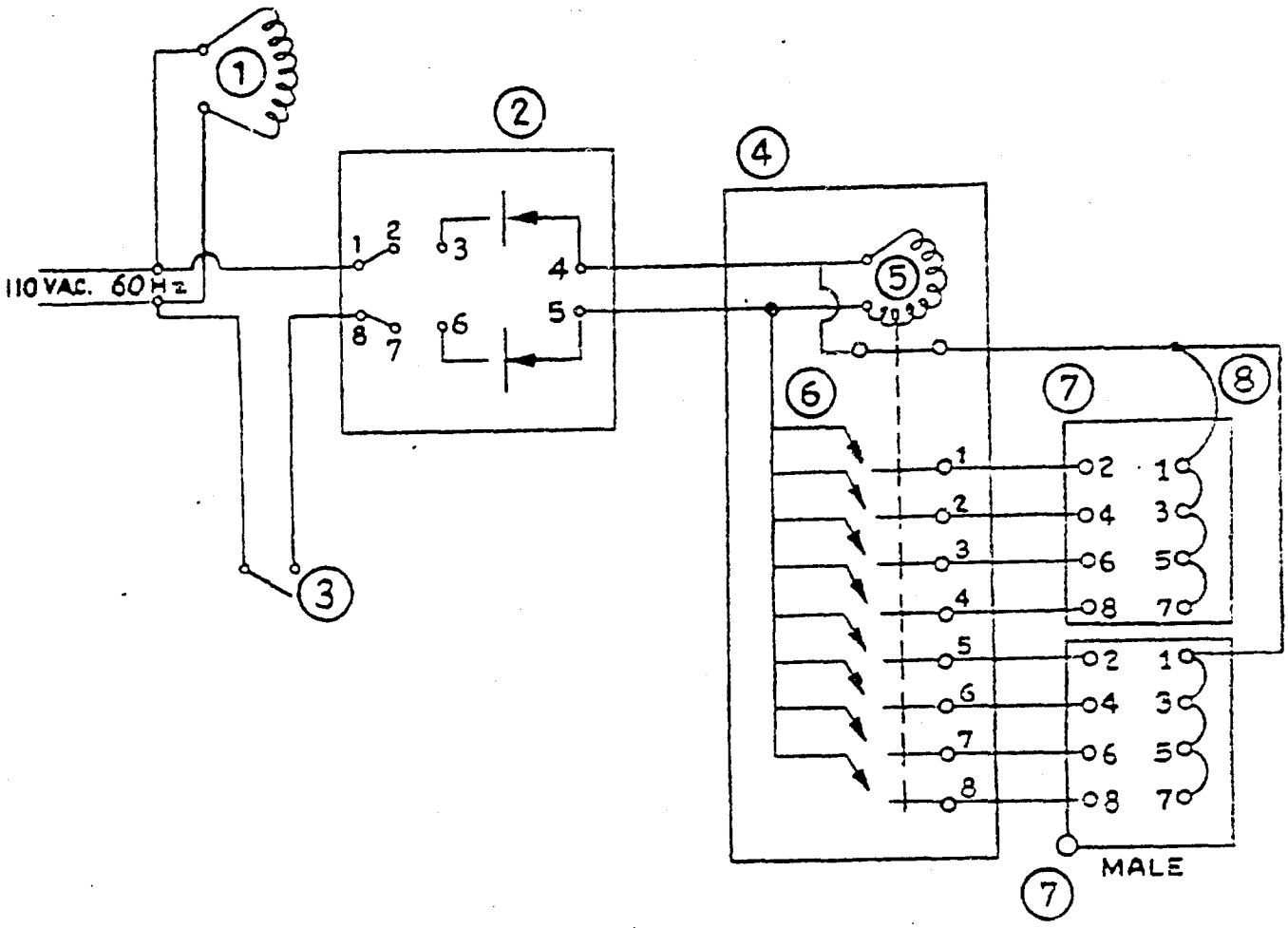

Fig. 3. Partial Schematic of Chassis Board

1. Blower motor
2. Delay relay, 0-180 sec, contacts for normally ON operation
3. Toggle switch with extension cord
4. Timer
5. Synchronous motor, 110v ac, 60-Hz
6. Cam operated microswitch
7. Eight-prong male plug
8. Common electrical line

(3) Coordinate as required and determine timing sequence for each cam.

(4) Set the cam timing sequence in the timer.

(5) Evacuate sample flasks.

(6) Transport sequential gas sampler and sampling personnel to launch area.

(7) Confirm sampler starting time.

(8) Place toggle switch in OFF position.

(9) Offset timer to compensate for confirmed sampler starting time prior to T = 0.

(10) Connect solenoid plugs to chassis board.

(11) Place sampler boxes in protected location within anticipated launch area.

(12) Place the free end of the remote sampling line at the desired location; for example, inside the launch vehicle crew compartment.

(13) Install manifold system. Use Teflon tape on all joints to assure airtight seal.

(14) Connect the coupling end of the line to the entry side of the manifold system.

(15) Connect blower motor with one-way check valve to the manifold system.

(16) Connect blower motor cord to the chassis board.

(17) Check all electrical connections.

(18) Check delay relay for proper interval.

(19) Connect power line to chassis board.

(20) Verify toggle switch is OFF.

(21) Connect power line to 110v ac power outlet.

(22) Give toggle switch to individual who will operate it.

(23) Vacate launch area of sampling personnel.

d. Sampler Activation. Place toggle switch in ON position at confirmed starting time.

e. Post-Firing Actions

(1) When access to the launch area is permitted, return sampling personnel to the sampler.

(2) Disconnect power line from source.

(3) Remove sampling line and manual trigger switch.

(4) Uncouple sampling line and blower motor from manifold system.

(5) Uncouple sampling boxes.

(6) Disconnect electrical lines from solenoid plugs and chassis board.

(7) Wind power cord on its reel.

(8) Account for all sampler equipment.

(9) Transport sequential gas sampler and sampling personnel away from launch area.

(10) Analyze gas samples.

5.6.4 Data Required

a. Timer offset in seconds

b. Timer settings in seconds

5.6.5 Data Reduction and Presentation: Not applicable. However, analysis of gas samples is accomplished primarily by infrared spectroscopy or as otherwise indicated.

5.7 Determination of Carbon Dioxide and Carbon Monoxide in Air by Infrared Spectroscopy (Missile Exhaust Gas Analysis)

5.7.1 Objective: Determine the carbon dioxide and carbon monoxide content of gas samples to establish extent of personnel hazard present

5.7.2 Standards: 5000 parts per million CO_2, 50 ppm CO

5.7.3 Method

a. Scope. This method is applicable for values of carbon dioxide and carbon monoxide above 10 ppm. Sample size must be 2 liters or larger.

b. Equipment Required

(1) Dual-beam infrared spectrophotometer

(2) Multiple path length cell, 10-meter

(3) Vacuum hose

(4) Vacuum pump

(5) Mercury manometer, 1 meter

(6) Barometer

(7) Metal and glass tee joints

(8) Stopcocks

(9) Sample bottles, 2-liter and 5-gallon

(10) Gas cylinder with known CO_2/CO concentration for standards

c. Preparation for Test. Install the multiple path length cell on the IR spectrophotometer. Energize the spectrophotometer and adjust for maximum transmission by checking the alignment of the multiple path length cell and attenuating the reference beam. Install chart paper and set instrument to 4 microns (2500 cm^{-1}). Set manual

slit width to 200 microns. Connect vacuum pump to one valve of multiple path length cell. Connect mercury manometer to other valve. Open valves. Evacuate multiple path length cell. Record manometer pressure. Record barometric pressure. Absolute cell pressure should be less than 5 mm Hg.

d. Conduct of Test

(1) Connect sample bottle to evacuated multiple path length cell. Open sample bottle valve. Open multiple path length cell valve. Open cell valve to manometer. Record manometer reading. Subtract from barometer reading. Record cell pressure. Close sample bottle valve. Close cell valve. Set wavelength to 4.0 microns. Adjust transmission to 80%. Scan and record to 4.5 microns (CO_2 peak occurs at 4.30 microns). Carbon dioxide level normally found in air ($\simeq$ 330 ppm) can be recorded at 1X. Carbon monoxide levels are usually much lower and normally will have to be recorded at 10X or 20X to give a discernible signal above background (CO peak occurs at 4.65 microns). Scan from 4.5 to 5.0 microns. Loosen scan drive and reset wavelength setting to 4.0 microns. Move chart to unused area. Tighten scan drive and repeat scan from 4.0 to 4.5 microns. Make appropriate settings and repeat scan from 4.5 to 5.0 microns. Repeat this procedure to obtain three replicate spectra of sample. To remove sample, connect vacuum pump to sample inlet valve of multiple path length cell. Open valve and evacuate cell to minimum pressure. Close valve. Cell is now ready for next sample.

(2) Repeat procedure in paragraph d(1) for each sample. Label each spectrum with sample identification, amplification scale, and cell pressure.

(3) Repeat procedure in paragraph d(1) for each standard gas. Pressure of gas standards in the multiple path length cell should match the pressure of the gas samples. Adjust cell pressure to match cell pressure when running samples. Standards selected should bracket sample values. Label spectra as in paragraph d(2).

5.7.4 Data Required

a. Retain spectra

b. Cell pressure in millimeters Hg for gas sample

c. Cell pressure in millimeters Hg for standard gas

d. Barometric pressure in millimeters Hg

e. Concentration in ppm CO_2/CO in standard gas

5.7.5 Data Reduction and Presentation

a. Draw a baseline for the absorption bands of each sample and standard as shown in Figure 4.

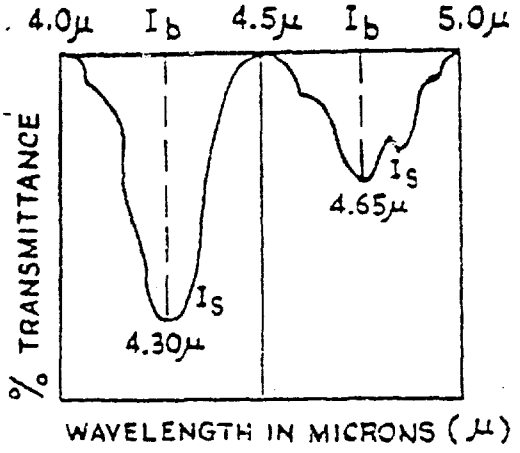

Fig. 4. Percent Transmittance Versus Wavelength

Legend:

I_b = percent transmittance of the baseline

I_s = percent transmittance of the absorption peak

b. Record the I_b (percent transmittance of the baseline) near the 4.30-micron and 4.65-micron wavelengths for each sample and standard.

c. Record the I_s (percent transmittance of the absorption peak) near the 4.30-micron and 4.65-micron wavelengths for each sample and standard.

d. Calculate and record the I_b/I_s ratio for each sample and standard absorption band.

e. Record and tabulate the absorption (Log (I_b/I_s)) for each absorption band.

f. Take the average absorption value for the CO and CO_2 peaks for the gas standards and plot concentration vs absorption.

g. Take the average absorption value for the CO and CO_2 peaks for the sample gas. From the plot, use the sample absorption values to interpolate sample concentration.

5.8 Determination of Hydrocarbons in Compressed Air by Infrared Spectroscopy

5.8.1 Objective: Measure the hydrocarbon content of air and other gases by infrared spectroscopy to establish extent of personnel hazard present

5.8.2 Standards: Five parts per million for compressed gas for breathing purposes

5.8.3 Method

a. Scope. This method is applicable to air and other gases containing more than 2 ppm hydrocarbons as hexane.

b. Equipment Required

(1) Dual-beam infrared spectrophotometer

(2) Multiple path length cell attachment for spectrophotometer, 10-meter

(3) Sample bottles, 5-gallon

(4) Vacuum pump with stopcock

(5) Stainless steel U-tube

(6) Sampler with firebrick packings

(7) Metal fittings and tubing

(8) Inert plastic tubing

(9) Drying tube

(10) Liquid nitrogen

(11) Widemouth Dewar flask, 2 quart

(12) Mercury manometer, 1 meter

(13) Flowmeter

c. Preparation for Test

(1) Construct collection train. See Figure 5.

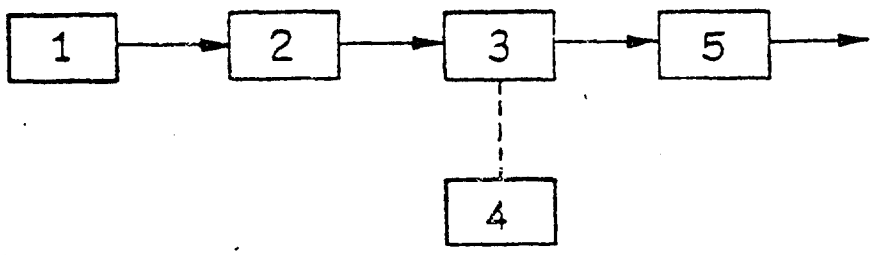

Fig. 5. Block Diagram of Collection Train

1. Sample source

2. Drying tube packed with Ascarite and a plug of drying agent

3. 1/2-inch outside diameter, 20-inch long, stainless steel U-tube packed to a depth of 3 inches in both arms with 30-60 mesh C-22 fire brick with valves and fittings on both ends

4. Two-quart, widemouth Dewar flask

5. Calibrated gas flow meter

(2) Prepare standards. Evacuate a clean 5-gallon gas collection bottle to less than 1 mm Hg absolute pressure. Use a precision, 10-microliter syringe to place 1 microliter (0.6603 mg) of n-hexane in the stopcock orifice. Open the stopcock and allow the collection bottle to fill to ambient pressure with air. The resulting concentration is 34 ppm hydrocarbons as hexane of weight in the bottle. Prepare other standards (2 microliters (68 ppm), 3 microliters (102 ppm)) in the same manner.

(3) Determine volume of multiple path length cell (equation 12. para 5.8.5a). Connect the manometer to the multiple path length cell. Connect the vacuum pump to the other valve. Energize the vacuum pump, open both cell valves, and evacuate the multiple path length cell. Record the manometer pressure. Record the barometric pressure. Absolute cell pressure should be less than 5 mm Hg. Close valve to vacuum pump. Remove connection to vacuum pump.

Connect a container of known volume (5 gallons or larger), whose internal pressure is known, to the multiple path length cell. Open valves between cell and the container and allow the manometer pressure reading to reach equilibrium. Record the manometer reading. Record the barometric pressure. Use equation 12 to calculate cell volume.

(4) Prepare instrument. Install the multiple path length cell on the IR spectrophotometer. Energize the spectrophotometer and adjust for maximum transmission by checking the alignment of the multiple path length cell and attenuating the reference beam. Install chart paper and set instrument to 3 microns (3333 cm^{-1}). Set manual slit width to 100 microns. Evacuate multiple path length cell and record manometer pressure. Record barometer pressure. Absolute cell pressure should be less than 5 mm Hg.

d. Conduct of Test

(1) Connect collection train to sample source. Slowly add liquid nitrogen to the Dewar flask to within 1/2 inch of the top. Open valves on sample source and U-tube. Through the U-tube, adjust sample flow to 3 liters per minute and pass approximately 60 liters.

NOTE: KEEP THE U-TUBE IN THE LIQUID NITROGEN DURING THE PERIOD OF SAMPLE COLLECTION ONLY. DO NOT ALLOW THE OPEN U-TUBE TO REMAIN IN THE LIQUID NITROGEN WITHOUT SAMPLE FLOW.

At the end of the sampling period, while the U-tube is still in the liquid nitrogen, close the valves at each end of the U-tube. Remove the U-tube from the liquid nitrogen. Place the U-tube in a beaker water bath at 80° to 90°C for 10 minutes before making the transfer to the multiple path length cell. Evacuate the cell and close the valves to the pump and manometer. Open the valve between U-tube and the multiple path length cell. Close the valves and open the outside valve on the U-tube. Allow the tube to fill with air. Close the outside valve and open the valves between the cell and the U-tube until the pressure has been equalized. Repeat this procedure until the pressure in the cell and U-tube are close to atmospheric pressure. Finally, open both valves on the U-tube and the sample inlet valve on the cell and allow the system to reach atmospheric pressure.

(2) Set wavelength to 3.0 microns. Adjust transmission to 80%. Scan and record to 4.0 microns. (Hydrocarbon peak occurs at 3.42 3.4 microns.) Loosen scan drive and reset wavelength setting to 3.0 microns. Move chart to unused area. Tighten scan drive and repeat scan between 3 and 4 microns. Repeat this procedure to obtain three replicate spectra of sample. Remove sample. Connect vacuum pump to sample inlet of multiple path length cell. Open valve and evacuate cell to minimum pressure. Close valve. Cell is now ready for next sample.

(3) Repeat procedure in paragraph d(2), above, for each sample. Label each spectrum with sample identification, amplification scale, and cell pressure.

(4) Repeat procedure in paragraph d(2), above, for each standard. Adjust cell pressure to match cell pressure when running samples. Select standards to bracket sample values. Label spectra as in paragraph d(3), above.

(5) Repeat procedure in paragraph d(2), above, to run blank on dry ambient air. Label as in paragraph d(3), above.

5.8.4 Data Required

a. Determine Volume of Multiple Path Length Cell

(1) Original pressure in millimeters Hg of the container

(2) Volume of the container in liters to nearest 0.1 liter

(3) Pressure in millimeters Hg of cell and container at equilibrium

b. Determine Hydrocarbon in Air

(1) Retain spectra of samples and standards.

(2) Cell pressure in millimeters Hg for samples

(3) Cell pressure in millimeters Hg for standards

5.8.5 Data Reduction and Presentation

a. Calculate the multiple path length cell volume. Use the formula:

$$Vc = Va\left(\frac{Pa}{Pc} - 1\right) \qquad (12)$$

where Pa = the original pressure of the container

Pc = the pressure of the cell and container at equilibrium

Va = the volume of the container

Vc = the volume of the multiple path length cell

b. Calculate the hydrocarbon content in air.

(1) Draw a baseline for the absorption bands of each sample and standard. See Figure 6.

(2) Determine the I_b (percent transmittance of the baseline) near the 3.42-micron wavelength for each sample, standard, and blank.

(3) Determine the I_s (percent transmittance of the absorption peak) near the 3.42-micron wavelength for each sample, standard, and blank

(4) Calculate and record the I_b/I_s ratio for each sample, standard, and blank absorption band.

(5) Record and tabulate the average absorption (log (I_b/I_s)) for each absorption band.

(6) Plot concentration versus average absorption for the standards.

(7) From the plot, use average sample absorption values to interpolate sample cell concentration.

(8) Use the sample cell concentration in the formula:

$$HC_T = \frac{\text{Sample Cell Concentration} \times \text{Cell Volume}}{\text{Original Sample Volume}} \qquad (13)$$

where HC_T = the hydrocarbon content of the original sample

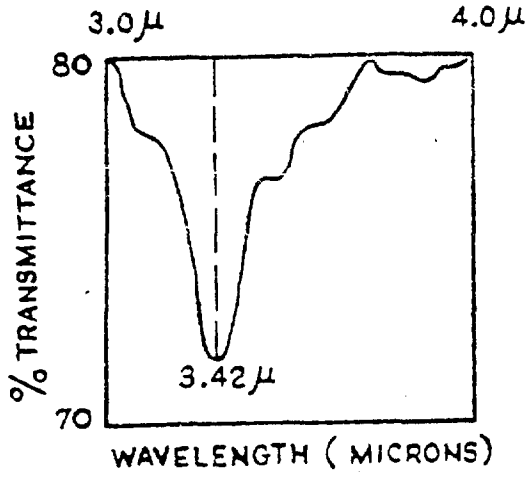

Fig. 6. Hydrocarbon Absorption Spectra

5.9 Determination of Fluoride in Drinking Water by the Specific Ion Electrode Method

5.9.1 Objective: Determine the fluoride ion concentration in drinking water

5.9.2 Standards: Between 0.7 to 1.2 parts per million

5.9.3 Method

a. Scope. The specific ion electrode (SIE) method is applicable to drinking water.

b. Equipment Required

(1) Potentiometric recorder, volt/millivolt range

(2) Fluoride specific ion electrode

(3) Calomel electrode

(4) pH meter

(5) Single-pan analytical balance, 0-200 gm ± 0.1 mg

(6) Double-pan laboratory balance, 0-2000 ± 0.1 gm

(7) Glassware:

Beakers, 250, 1000 ml

Volumetric flasks, 100, 1000 ml

Pipets, 1, 2, 10, 50 ml

Graduated cylinders, 100 ml

Polyethylene bottles, 1000 ml

Weighing boats

c. Preparation of Reagents

(1) Ionic strength adjustment buffer. Place 500 ml distilled water in a 1000-ml beaker. Add 57 ml glacial acetic acid, 58 gm of NaCl, and 0.30 gm sodium citrate. Stir to dissolve. Place beaker in water bath (for cooling). Insert pH and reference electrodes in solution. Slowly add 5M NaOH (200 gm/lt), and adjust pH between 5.0 and 5.5. Cool to room temperature. Transfer to 1000-ml flask and add distilled water to the mark.

(2) Fluoride ion standard solution (1000 ppm F^-). Dissolve 2.2101 gm NaF in a 1000-ml volumetric flask with distilled water. Dilute to the mark. Transfer to 1000-ml polyethylene bottle.

WARNING: NaF IS A TOXIC MATERIAL AND MUST BE HANDLED CAREFULLY. AVOID BREATHING NaF DUST. CLEAN UP WORK AREA AND WASH HANDS AFTER PREPARING NaF SOLUTION.

(3) Fluoride ion working standard (100 ppm F^-). Pipet 10 ml of 1000 ppm F^- solution into a 100-ml volumetric flask. Dilute to the mark with distilled water.

NOTE: PREPARE FRESH FLUORIDE ION WORKING STANDARDS AT THE TIME OF ANALYSIS.

(4) Fluoride ion working standard (1 pmm F^-). Pipet 1 ml of 100 ppm F^- solution into a 100-ml volumetric flask. Pipet 50 ml of ionic strength adjustment buffer into the 100-ml flask. Dilute to the mark with distilled water.

(5) Fluoride ion working standard (2 ppm F^- or N ppm F^-). Pipet 2 ml (or N ml) of 100 ppm F^- solution into a 100-ml volumetric flask. Pipet 50 ml of ionic strength adjustment buffer into the 100-ml flask. Dilute to the mark with distilled water.

d. Preparation of Equipment. Check potentiometric recorder for proper operation. Check reference and specific ion electrodes and connect them to the recorder. Zero the recorder. Place the electrodes in distilled water.

e. Determination of Fluoride Ion

(1) Pipet 50 ml of the water sample into a 100-ml volumetric flask. Dilute to the mark with ionic strength adjustment buffer.

(2) Transfer the 1 ppm fluoride ion working standard solution to a 250-ml beaker. Place the electrodes in the standard solution and gently stir the solution. Allow the voltage reading to stabilize. Label the recorder trace. Remove the electrodes from the solution. Pour the solution back into its original flask. Rinse the electrodes with distilled water; then gently blot dry with soft tissue.

(3) Repeat step (2) above for each subsequent fluoride ion working standard.

(4) Repeat step (2) above for each sample.

NOTE: THE VOLTAGE READINGS FOR THE STANDARD SHOULD BRACKET THE VOLTAGE READINGS FOR THE SAMPLE. IF THIS IS NOT SO, PREPARE AND MEASURE ADDITIONAL STANDARDS OF THE APPROPRIATE CONCENTRATIONS.

5.9.4 Data Required

a. Voltage readings for samples

b. Voltage readings for standards

c. Concentration of standards in ppm

d. Original volume of sample in milliliters

e. Volume of buffered sample solution in milliliters

5.9.5 Data Reduction and Presentation

a. Plot the values for the standard solutions on semilogarithmic graph paper with the voltage readings on the linear scale and the concentration values on the logarithmic scale. The plot should be a straight line. Locate the sample voltage readings on the plot and determine the sample fluoride solution concentration.

b. Multiply this graphical value by the dilution factor to obtain the F^- concentration in the sample. Use the formula:

F^- concentration =

$$\text{graphical value} \cdot \frac{\text{Volume of Buffered Sample Solution}}{\text{Original Sample Volume}} \qquad (14)$$

5.10 Determination of Oxygen by Nondestructive Neutron Activation Analysis

5.10.1 Objective: Determine the oxygen content in various solid samples by nondestructive neutron activation analysis, to monitor changes in oxygen content as influenced by sample environment

5.10.2 Standards: Not applicable

5.10.3 Method

a. Scope. This method has been developed for solid samples weighing between 10 and 50 gm, containing from 1 to 15 gm of oxygen. However, the samples must not be explosive materials and, moreover, the samples should not contain fluorine.

b. Equipment Required.

(1) High-intensity source of neutrons with energy greater than 10 million electron volts

(2) A system for rapidly transferring samples between the irradiation and counting sites

(3) A rotation device with positions for two samples and capable of direct connection to the rapid transfer system

(4) A gamma-ray scintillation spectrometry system with two counting stations

(5) Sample containers of polyethylene (or similar nonoxygen and nonfluorine containing plastic) suitable for use in the rapid-transfer system

(6) A programming device for controlling the cycle of transfer to irradiation site, irradiation, transfer to counting site, and counting

c. Preparation of Standard and Sample.

(1) Choose a powdered standard which contains no fluorine.

(2) Reduce solid sample to a powder.

(3) Dry standard and sample in oven at 105°C for about 1 hour.

(4) Remove standard and sample from oven, place in a dessicator, and cool to room temperature

(5) Weigh empty sample containers with lids. Record weight.

(6) Compact the standard into a container. Screw in container lid so that it tightly compacts the standard. Weigh the container. Record weight. Treat the sample in the same manner as the standard.

d. Preparation of Pneumatic Transfer System. Check to make sure there is ample compressed nitrogen to drive the standard/sample containers quickly through the transfer system. See Figure 7.

e. Preparation of Sample Rotation Device. Place the rotation device flush with the target end of the neutron generator, so that the maximum neutron flux will strike standards/samples during irradiation. See Figure 7.

f. Preparation of Neutron Generator. Operate the neutron generator according to installation safety directives and the instrument manual. Check that the tritium content of the target is adequate to give a total neutron production rate of at least 10^{10} neutrons per second. See Figure 7.

g. Preparation of the Counting System.

(1) Calibrate each analyzer so as to count only the gamma rays with energies above 5 million electron volts. Use calibration procedures contained in appropriate operating manuals.

(2) Determine the relative counting efficiencies of the two counters. Irradiate two samples of the same composition. Cycle the samples and record the final number of counts from each counter. Repeat this procedure eight times, or until confidence in the value of relative counting efficiencies is established.

NOTE: FOR SAMPLES OF THE SAME COMPOSITION AND WEIGHT, THE RELATIVE NUMBERS OF OBSERVED COUNTS IN THE TWO COUNTERS WILL BE EQUAL TO THE RELATIVE COUNTING EFFICIENCIES OF THE TWO COUNTERS.

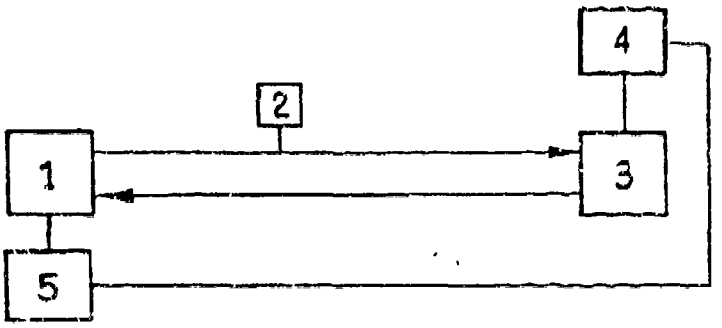

Fig. 7. Block Diagram of Neutron Activation Analysis Test Setup.

Legend:

1. Counting Stations. Each station consists of at least one NaI(Tl) scintillation crystal connected to a pulse height analyzer.

2. Pneumatic Transfer System. Consists of two flexible tubes which transfer samples from the counting stations to the irradiation site and then back to the counting stations.

3. Sample Rotation Device. The irradiation terminal for the two pneumatic tubes. It is capable of holding two samples and rotating each simultaneously about two axes: (1) end-over-end about an axis in line with the deuteron beam of the neutron generator and (2) about the cylindrical axis of the sample itself.

4. Source. High-intensity source of neutrons with energy greater than 10 million electron volts (Mev)

5. Programmer. This is a device for controlling the cycle of transfer to irradiation site, irradiation, transfer to counting site, and counting.

(3) Determination of the Background Counting Rate. Take counts with no samples in the counters. If these background rates are less than 0.5 percent of the observed counting rates for the irradiated samples, make no correction. If the background counting rate exceeds this value, subtract the product of the background counting rate and the time of counting from the number of counts for the irradiated sample. Use the formula:

$$C_c = C_i - \left(\frac{C_b}{\text{min}} \times Ti\right) \qquad (15)$$

where C_c = corrected count

C_i = counts for irradiated samples

C_b/min = counts with no samples in the counters divided by time of background count

Ti = counting time for irradiated samples

h. Preparation of the Programmer. Determine by trial the pneumatic pressure and blow time which are adequate to transfer standard/sample containers to and from the rotation device without jamming.

NOTE: A TYPICAL CYCLE WOULD INVOLVE A BLOW TIME TO IRRADIATION OF 2 SECONDS, AN IRRADIATION TIME OF 30 SECONDS, A BLOW TIME TO COUNTER OF 2 SECONDS, AND A COUNTING TIME OF 60 SECONDS.

i. Discussion of Neutron Activation Analysis Test Setup (See Figure 7). A sample of known oxygen content and one of unknown oxygen content are pneumatically transferred to a rotation device which is positioned next to a deuterium-tritium generator of 14-Mev neutrons. Oxygen is activated by the neutrons to give radioactive nitrogen-16. After irradiation, the activated samples are quickly transferred to radiation containers where the radiations from nitrogen-16 are selectively counted by means of gamma-ray scintillation spectrometry. The entire procedure of transferring, irradiation, and counting requires less than 3 minutes. From the oxygen content of the known and the observed counting data, the oxygen content of the unknown can be calculated.

j. Conduct of Test.

(1) Load sample and standard into the pneumatic transfer system.

(2) Press reset buttons on scalers. Set counts at zero.

(3) Start cycle. Press programmer button.

(4) Record final number of counts from each counter.

(5) Calculate the ratio of counts in the two counters.

(6) Repeat operations (2) through (5) five to ten times to make sure that the calculated ratio is consistent and within a relative standard deviation of about 2 percent given by the ratio:

$$\frac{\sigma}{\mu} \times 100 \simeq 2\% \qquad (16)$$

where σ = standard deviation

μ = mean value

Use standard methods to reject individual values that are statistically out of line.*

(7) Remove samples from the transfer system in accordance with installation safety directives.

5.10.4 Data Required: Weights in grams to the nearest 0.0001 gram; time in minutes to the nearest 0.01 minute

a. Weight of container 1 for standard

b. Weight of container 1 plus standard

c. Weight of container 3 for comparison standard

d. Weight of container 3 plus comparison standard

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*See Dixon, W. J., and F. J. Massey. Introduction to Statistical Analysis, Chapter 6, New York: McGraw Hill.

e. Weight of container 2 for sample

f. Weight of container 2 plus sample

g. Oxygen content of standard

h. Diameter of sample in centimeters to nearest 0.1 cm

i. Volume of sample in cubic centimeters to nearest 0.1 cm^3

j. Number of counts for standard

k. Number of counts for unknown sample

l. Time of irradiation for sample and standard

m. Time of background count

5.10.5 Data Reduction and Presentation

a. Calculate the ratio of counts in the two counters. Use the formula:

$$R_c = \frac{C_u}{C_s} \tag{17}$$

where R_c = the ratio of counts in the two counters

C_u = the number of counts for the unknown (sample counter)

C_s = The number of counts for the standard (standard counter)

b. Calculate the counting efficiency of the counter in which the standard is counted relative to that in which the unknown sample is counted. For samples of the same composition and nearly the same weights (para 5.10.3g(1)), use the formula:

$$R_e = \frac{W_c}{W_s \times R_c} \tag{18}$$

where R_e = the counting efficiency of the counter in which the standard is counted relative to that in which the unknown sample is counted

W_c = weight of comparison standard in sample counter

W_s = weight of standard in standard counter

R_c = ratio of counts in the two counters, as in equation 17

c. Calculate the correction for self-shielding of neutrons by the sample. Use the formula:

$$\text{SS corr} = 1 + ((SS)_u - (SS)_s) \times F_{ss} \quad (19)$$

where SS corr = the correction for self-shielding of neutrons by the sample

$(SS)_u$ = the self-shielding factor for the unknown sample (See para d, below.)

$(SS)_s$ = the self-shielding factor for the standard (See para d, below.)

F_{ss} = an empirical factor. Use the value 0.023. (To determine F_{ss} experimentally, run a series of standards against each other. Calculate the value of F_{ss} which gives the best fit between known and experimentally calculated oxygen content.)

d. Calculate $(SS)_s$ and $(SS)_u$. Use the formula:

$$SS = D \times \Sigma_T \quad (20)$$

where SS = the self-shielding factor (unitless)

D = the diameter of the sample in centimeters

Σ_T = the macroscopic total cross section for 14-Mev neutrons in cm^{-1}

e. Calculate Σ_T. Use the formula:

$$\Sigma_T = \frac{1}{V}\Sigma_i \sigma_{T(14\ Mev)_i} \frac{Wi}{Mi} \times NA \qquad (21)$$

where Σ_T = the macroscopic total cross section for 14-Mev neutrons in cm^{-1}

V = the volume of the sample

Wi = the weight of element i in grams

Mi = the atomic weight of element i in grams per mole

$\sigma_{T(14\ Mev)_i}$ = the microscopic total cross section for 14-Mev neutrons in cm^2

$NA = 6.02 \times 10^{23}$ atoms per mole

f. Calculate the correction for self-absorption of emitted gamma rays in the sample. Use the formula:

$$(SA)\ corr = (SA)_s/(SA)_u \qquad (22)$$

where $(SA)_s$ = the self-absorption factor for the standard (See para g, below.)

$(SA)_u$ = the self-absorption factor for the unknown sample (See para g, below.)

g. Calculate $(SA)_s$ and $(SA)_u$. Use the formula:

$$SA = \exp(-\overline{\mu l}\frac{W}{V}a) \simeq 1 - \overline{\mu l}\frac{W}{V}d \qquad (23)$$

where SA = the self-absorption factor

exp = base of natural logarithms (2.71828 . . .)

$\overline{\mu l}$ = the average absorption coefficient for 6- to 7-Mev gamma rays in square centimeters per gram. (Use 0.03 cm^2/gm for samples containing only elements with atomic numbers less than 53. Use 0.04 cm^2/gm for samples containing elements with atomic numbers greater than or equal to 53.)

W = the weight of the sample

V = the volume of the sample

d = the average path length of gamma rays (Use d = 0.55D, where D is the diameter of the sample.)

h. Calculate the oxygen content of the sample. Use the formula:

$$O_x = R_c \times R_e \times \frac{W_{os}}{W_u} \times (\text{SS corr}) \times \text{SA corr} \times 100 \qquad (24)$$

where O_x = percent oxygen content by weight

R_c = the ratio of counts in the counters (equation 17, para 5.10.5a)

R_e = the relative counting efficiency of the counters (equation 18)

W_{os} = the weight in grams of oxygen in the standard (oxygen content of standard × weight standard)

W_u = the weight of the unknown sample

SS corr = the self-shielding correction (equation 19)

SA corr = the self-absorption correction (equation 22)

5.11 Determination of Nitrobenzene in Aniline by Polarography

5.11.1 Objective: To determine the nitrobenzene content of aniline to establish its purity

5.11.2 Standards: Nitrobenzene content in aniline should be less than 0.2 percent by weight.

5.11.3 Method

a. Scope. This procedure allows for the determination of nitrobenzene in aniline in concentrations from 0.5 percent to less than 0.001%.

b. Equipment Required

(1) Polarograph

(2) H-cell and dropping mercury electrode assembly

(3) Single-pan analytical balance, 0-200 gm ± 0.1 mg

(4) Triple-distilled mercury

(5) Gas washing bottle

(6) Oxygen-free nitrogen

(7) Glacial acetic acid, reagent grade

(8) Double-distilled water

(9) Nitrobenzene, reagent grade

(10) Four weighing bottles, 30 mm × 60 mm

(11) Volumetric pipets, 5, 10, 15 ml

(12) Microsyringe, 8-10 microliter capacity

(13) Ring stand, ring, test tube clamps, test tube, tubing

c. Preparation for Test

(1) Supporting Electrolyte. Pipet 250 ml glacial acetic acid into a 500-ml volumetric flask. Dilute to the mark with double-distilled water. Mix well by shaking and inverting.

(2) Working Solutions. Weigh four 30 mm × 60 mm weighing bottles with stoppers in place. Record weight; then pipet 10 ml of aniline (fuel sample) into each. Reweigh to determine the weight of aniline (fuel sample) added. With a microsyringe, add about 5 microliters of reagent grade nitrobenzene to the first bottle, about 10 microliters to the second bottle, and about 15 microliters to the third bottle. Mix by gently swirling and reweigh to determine the weight of nitrobenzene added. Determine percentage of nitrobenzene added to fuel samples. Use equation 25. Add nothing to the fourth bottle.

d. Conduct of Test

(1) Set up apparatus as shown in Figure 8. Adjust mercury drop time to 3 seconds.

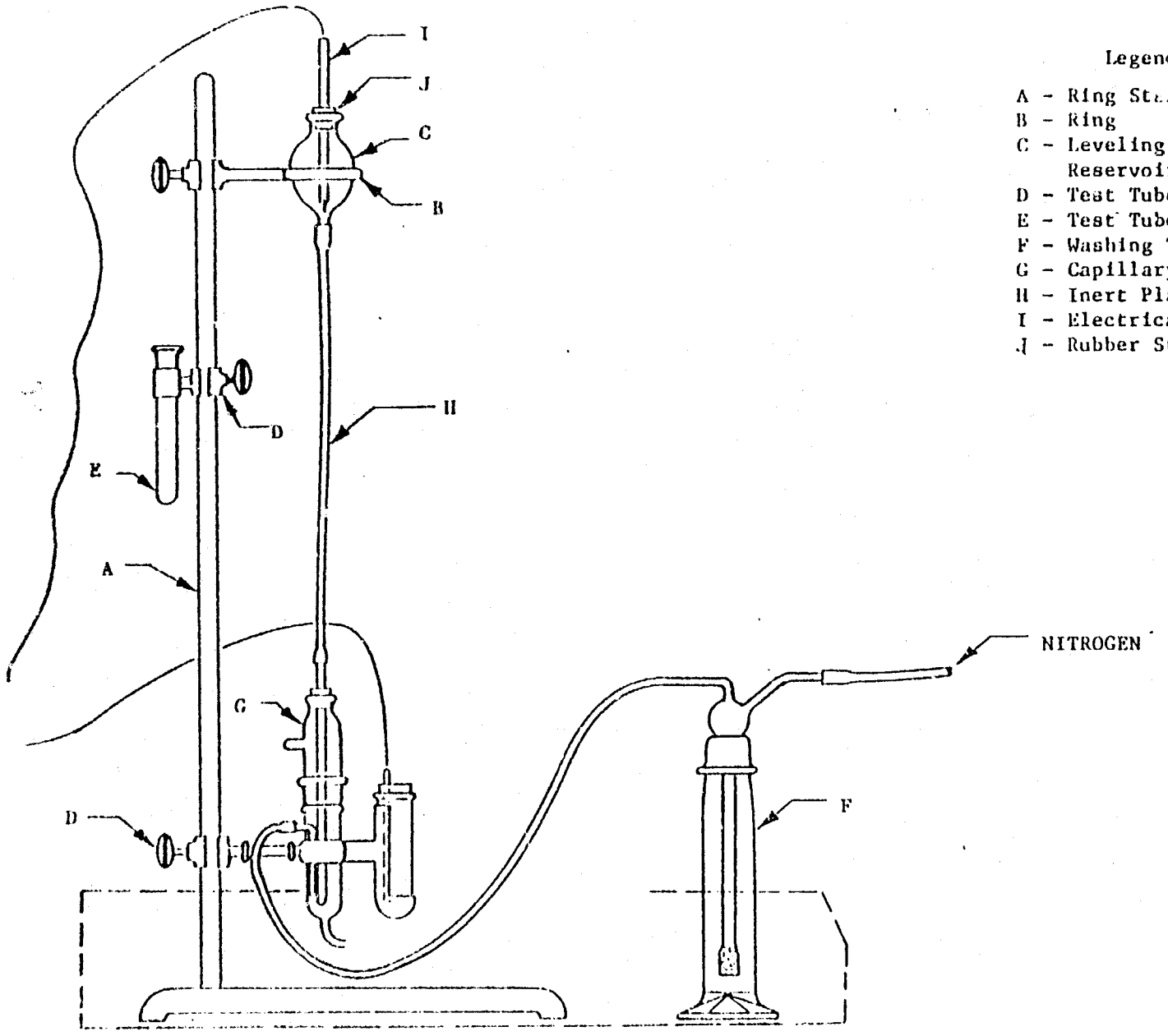
(2) Turn on power switch on the polarograph and allow instrument to warm up for at least 15 minutes.

(3) Drain the sample compartment of the H-cell and rinse with double-distilled water. Wipe the compartment dry with a clean, lint-free tissue and pipet in 15 ml of 50 percent acetic acid and 5 ml of solution to be analyzed. Bubble nitrogen through the solution for about 15 minutes to deaerate; then turn nitrogen off.

NOTE: DURING DEAERATION, THE CAPILLARY ASSEMBLY SHOULD BE IN PLACE ON THE ELECTROLYSIS CELL AND MERCURY SHOULD BE FLOWING.

(4) Turn "voltage range" switch on polarograph to "0 to -2" volts. Turn "cell" switch to "R_S;" turn "current sensitivity" knob to "0.2" or "0.3."

(5) Standardize the instrument. Turn "operation" knob to "chart release." Turn center "standardization" knob to the current side and adjust the "current" knob until the pen movement just ceases.



Legend

A - Ring Stand
B - Ring
C - Leveling Bulb (Mercury Reservoir)
D - Test Tube Clamp
E - Test Tube
F - Washing Tower
G - Capillary H-cell Assy
H - Inert Plastic Tubing
I - Electrical Connection
J - Rubber Stopper

Fig. 8. Dropping Mercury Electrode Assembly

Turn center "standardization" knob to the voltage side and adjust the "voltage" knob until the pen movement just ceases. The instrument is now standardized.

(6) Determine the proper setting of the current sensitivity knob. Turn "operation" knob on the polarograph to "chart release." Turn "cell" switch to "normal polarity." Turn "R. C. damping" knob off. Turn "voltage applied" knob to "O." Turn "current sensitivity" knob to 0.2 or 0.3. Adjust the pen to zero on the chart. Use upper and lower displacement knobs as required. Turn "voltage applied" knob to "50%," and adjust the "current sensitivity" knob until a deflection of about 200 mm is obtained on the chart.

(7) Recheck standardization. Turn "cell" switch to "R_s" and repeat operation (6) above.

(8) Turn "cell" switch to "normal polarity" and "voltage applied" switch to "O." If pen does not go to the zero line on the chart, adjust the upper "displacement" knob until it does. Turn "voltage drive" switch to "0 - 100%" and "operation" knob to "record." Record until the "voltage applied" knob has rotated to "50%." Then turn "operation" knob to "standby."

(9) Repeat steps (3) through (8) above with all four solutions.

(10) When the last solution has been analyzed, turn "power" switch "off;" rinse sample compartment of the H-cell with double-distilled water. Rinse capillary with double-distilled water and place in capillary storage tube. Fill sample compartment with double-distilled water and stopper.

5.11.4 Data Required

a. Polarograms

b. Current sensitivity setting

c. Weights in grams to nearest 0.0001 gm

d. Weight of weighing bottle (tare 1)

e. Weight of tare 1 plus aniline

f. Weight of tare 1 plus aniline plus 5 microliters nitrobenzene

g. Weight of weighing bottle (tare 2)

h. Weight of tare 2 plus aniline

i. Weight of tare 2 plus aniline plus 10 microliters nitrobenzene

j. Weight of weighing bottle (tare 3)

k. Weight of tare 3 plus aniline

l. Weight of tare 3 plus aniline plus 15 microliters nitrobenzene

m. Weight of weighing bottle (tare 4)

n. Weight of tare 4 plus aniline

5.11.5 Data Reduction and Presentation

a. Determination of Percent Nitrobenzene added

(1) Subtract tare weight from tare weight plus aniline plus nitrobenzene addition for each standard.

(2) Subtract the tare weight plus aniline from tare weight plus aniline plus nitrobenzene addition for each standard.

(3) Use the formula:

$$\% \text{ NBA} = \frac{\text{WT NB}}{\text{WT AN} + \text{NB}} \times 100 \qquad (25)$$

where % NBA = percent by weight of nitrobenzene added

NB = nitrobenzene

AN = aniline

b. Determination of Nitrobenzene in Aniline Sample

(1) Calculate diffusion current (id). Use the formula:

$$id = h \times CS \tag{26}$$

where id = diffusion current in microamperes

h = height of polarographic wave in millimeters

CS = current sensitivity setting (microamperes per millimeter)

(2) Calculate the diffusion current (id) for each of the four solutions. Then substitute in the formula:

$$\frac{\%\ NBA + X}{ids} = \frac{X}{idx} \tag{27}$$

where % NBA = the percent nitrobenzene added to standard (equation 25)

X = the percent nitrobenzene present in sample before additions

ids = the diffusion current of the standard

idx = the diffusion current of the sample with no additions

Solve equation 27 for each of the three unknowns and take the average as the percent nitrobenzene in the sample. See sample calculation c below.

c. Sample Calculation

(1) The following is an example of a typical analysis using the procedure in 5.11.3d.

(2) A sample solution known to contain approximately 0.002 to 0.003 percent nitrobenzene was analyzed. The solution was prepared from redistilled reagent-grade aniline and reagent-grade nitrobenzene. The supporting electrolyte was prepared from reagent-grade glacial acetic acid and dionized distilled water.

(3) The results of the experiment are shown in Table 5. The polarograph obtained is shown in Figure 9. The data showed the sample solution to be 0.00210 ± 0.0003 percent nitrobenzene.

TABLE 5

RESULTS OF EXPERIMENT – SAMPLE CALCULATION

	Solution Number			
	33	38	57	Sample
Weight of sample (grams)	10.1728	10.1627	10.1748	--
Weight nitrobenzene added (grams)	0.0042	0.0098	0.0144	--
Percent added nitrobenzene	0.04129	0.09643	0.1415	--
id (microamperes)	10.8900	24.3750	36.6000	0.5280
Percent nitrobenzene in sample as calculated from solution analyzed	0.00210	0.00214	0.00207	

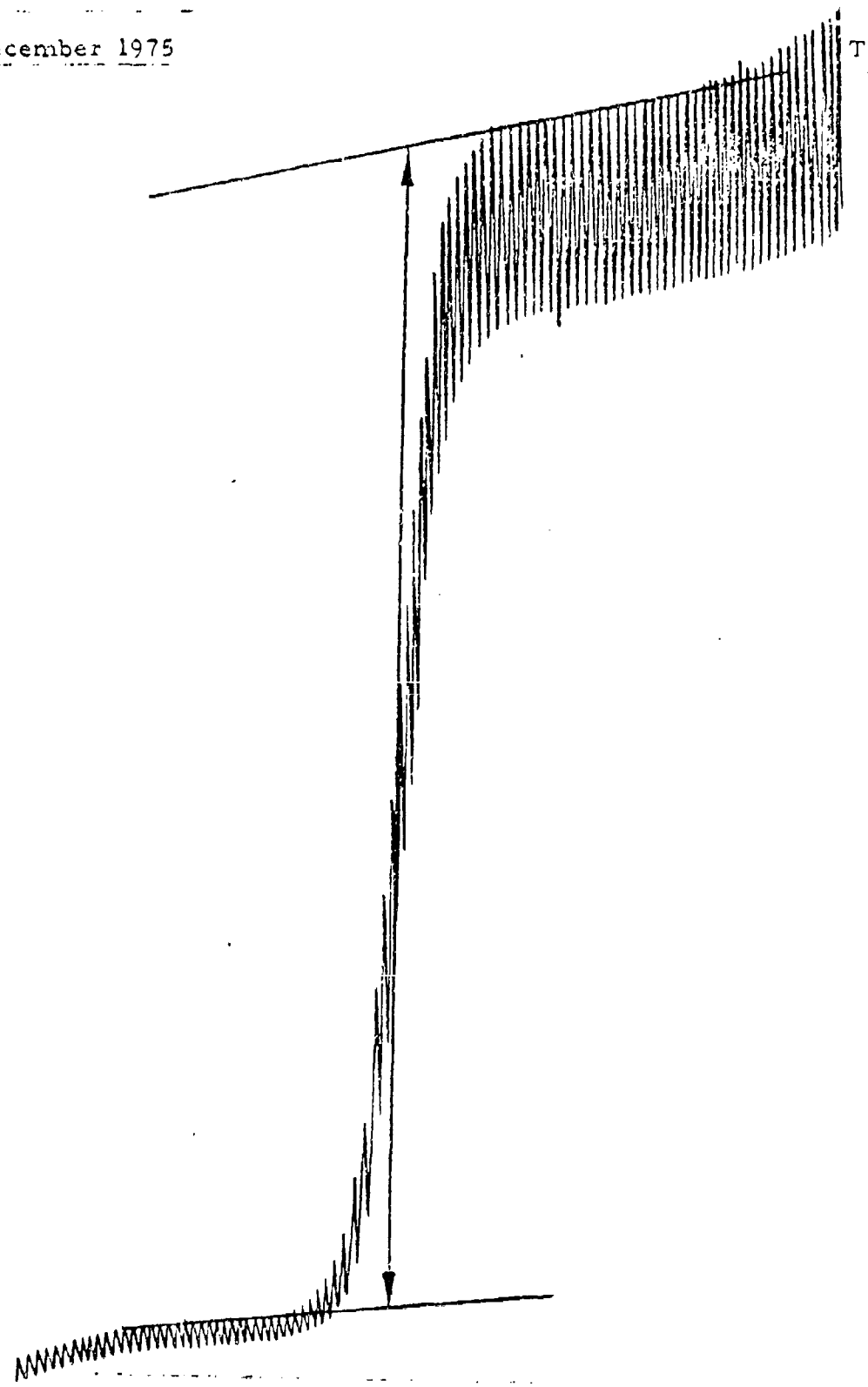


Fig. 9. Polarogram Solution Number 33; Current Sensitivity: 0.060 Microamperes per Millimeter

5.12 Determination of Copper in Water by Atomic Absorption Spectroscopy

5.12.1 Objective: To determine the copper content of water samples. Water used for environmental tests on unprotected aluminum surfaces must be low in copper because copper ions corrode aluminum by galvanic action.

5.12.2 Standards: The copper content should be less than 600 parts per billion (ppb).

5.12.3 Method

a. Scope. This method may be used to determine copper in the range of 20 to 300 ppb. The chelation and extraction employed in the procedure allow for the determination of lead, zinc, cadmium, and nickel on the same sample in the ppb range.

b. Equipment Required.

(1) Double-beam, grating atomic absorption spectrophotometer

(2) Sensibly monochromatic copper hollow cathode lamp source

(3) PH meter accurate to ± 0.1 pH unit

(4) Separatory funnels, 500-ml

(5) Class A 1000-ml, 100-ml, and 25-ml volumetric pipets

(6) Class A 25-, 10-, 5-, and 2-ml volumetric pipets

(7) Class A 1-ml serological pipets

(8) Analytical balance, 0-200 gms ± 0.1 mg sensitivity

(9) Double-distilled water. Use to prepare all reagents, standards, and as dilution water.

c. Preparation of Glassware. Rinse all glassware in 50 percent (V/V)HNO_3, followed by rinsing in distilled water.

d. Preparation of Reagents.

(1) Ammonium pyrrolidine dithiocarbamate (APDC) reagent, ACS grade. Dissolve 1.0 gram of APDC in 100 ml of distilled water.

(2) Methyl iso-butyl ketone (MIBK), ACS grade. Wash one volume of MIBK with 5 volumes of 1 percent (V/V) HCl. Remove excess acid by washing with distilled water. Perform these operations in a 500-ml separatory funnel.

(3) Prepare a stock standard of 1000 ppm Cu by dissolving 1.0000 grams of ACS grade copper in a min. of HNO_3. Quantitatively transfer to a 1-liter volumetric flask and dilute to volume.

(4) Prepare a 5-ppm Cu standard by 0.50 ml of the stock standard to 100 cc in a volumetric flask.

(5) Prepare working standards of 25, 50, 100, 150, and 200 ppb Cu by diluting 0.5, 1.0, 2.0, 3.0, and 4.0 ml, respectively, of the 5-ppm standard in separate volumetric flasks.

(6) Acidify 100 cc of sample(s) and working standards to a pH of 3.0, with dilute HCl. This allows for the chelation and extraction of copper, lead, zinc, cadmium, and nickel on the same sample.

(7) Transfer the acidified sample(s) to a separatory funnel. Add 5 cc of APDC reagent and 10 cc of MIBK. Shake manually for 2 minutes, allow the layers to separate, remove the MIBK layer and save for analysis.

(8) Perform the operation in step 7 for each standard.

(9) The sensitivity may be increased by using larger sample volumes and/or smaller MIBK washings. The standards should be the same volume as the sample, to eliminate correction factors.

e. Conduct of Test.

(1) Warm up the instrument and set the operating parameters for the analysis.

(2) Aspirate the 5 ppm Cu standard and optimize all operating parameters for maximum absorption.

(3) Aspirate clean MIBK and null the instrument

(4) Aspirate the sample(s) and record the percent absorption

(5) Repeat step 4 for the standards. The analysis should be conducted in triplicate, at a minimum, and the percent absorption averaged for each sample and standard.

5.12.4 Data Required

a. Average the percent absorption for standards and sample(s).

b. Convert the percent absorption to absorbance.

5.12.5 Data Reduction and Presentation

a. Plot the absorbance of the standards versus concentration of the standards on Cartesian coordinate paper. This is the working curve.

b. Read the concentration of the sample(s) from the working curve.

5.13 Determination of Triethylamine in Furfuryl Alcohol by Gas Chromatography

5.13.1 Objective: To determine the percent by weight of triethylamine in furfuryl alcohol. Deterioration of furfuryl alcohol due to auto-oxidation is indicated by the development of color, acidity, and increased moisture content, which may be inhibited by the addition of triethylamine (TEA) or other basic material.

5.13.2 Standards: Paragraph 3.3 of MIL-P-45702C (USAF) states that 0.2 ± 0.05 percent TEA shall be added to each accepted lot of furfuryl alcohol; however, no applicable test method is given.

5.13.3 Method

a. Scope. This method is applicable to furfuryl alcohol containing 0.2 ± 0.05 TEA by weight.

b. Equipment Required.

(1) Dual-column gas chromatograph with thermal conductivity detector (TCD)

(2) Flint glass weighing bottles

(3) Syringes, ten microliter

(4) Spectographic grade TEA

(5) Analytical balance, 0.1 mg accuracy, ± 0.05 mg sensitivity

(6) Helium as carrier gas for the gas chromatography (GC) determination

(7) Six-foot coiled column of 15 percent silicone oil DC-200 on 80-100 mesh Chromasorb W (two each)

(8) Recorder for GC, 0-5 MV span

(9) Class A 3.0 ml volumetric pipets

c. Preparation of Standards.

(1) Pipet 3.0 ml of the furfuryl alcohol sample to three tared weighing bottles.

(2) Weigh to the nearest 0.0001 gm

(3) Add 10, 20, and 30 microliters of TEA, respectively, to three weighing bottles and mix well.

(4) Weigh to the nearest 0.0001 gm.

(5) Determine the percent by weight TEA added from the formula below:

$$\% \text{ TEA added} = \frac{\text{Wt TEA added}}{\text{Total Wt Sample}} \times 100 \qquad (28)$$

d. Operation of Equipment.

(1) Ensure that the carrier gas is flowing to the detector.

(2) Set the following operating parameters:

Column Temperature	120°C
Injector Temperature	155°C
Detector Temperature	200°C
Detector Current	250 ma
Helium flow	25 cc/min

(3) The above parameters may be varied to enhance the analysis with the particular GC used.

(4) Allow the GC to stabilize.

e. Conduct of Test.

(1) Condition the columns by injecting 10 microliters of one standard.

(2) Allow for complete sample elution.

(3) Start the recorder.

(4) Trace a noise-free baseline for about 5 minutes.

(5) Withdraw 4.0 microliters of the sample, wipe off any excess sample from the needle, and quickly inject into the column port.

(6) The TEA emerges with a R_T of about 1.6 minutes.

(7) When the furfuryl alcohol emerges, turn off the recorder and allow the sample to elute completely. This usually takes about 20 minutes.

(8) Repeat the above sequence for the standards.

(9) New columns may have to be conditioned to obtain good resclution.

5.13.4 Data Required: Measure the peak heights obtained for the sample and standards.

5.13.5 Data Reduction and Presentation

a. Subtract the peak height of the sample from the standards. This is necessary because the standards were prepared by standard addition.

b. Construct a working curve by plotting peak height versus concentration.

c. Determine the value of the sample from the working curve.

5.14 Determination of Chromium and Nickel in Stainless Steels by X-ray Spectroscopy

5.14.1 Objective: To determine the chromium and nickel content of stainless steels. The amount of chromium and nickel alloyed with iron imparts corrosion resistance to the metal and serves as a means of distinguishing the three major classes of stainless steels.

5.14.2 Standards: Certified NBS spectrographic stainless steel standard discs 1-$\frac{1}{4}$ inch in diameter and $\frac{1}{4}$ inch thick. These standards should bracket the range of the suspected sample composition. The standards selected should match the composition of the sample as closely as possible, to minimize error due to matrix effects.

5.14.3 Method

a. Scope. This method may be used to analyze the chromium and nickel content in the three major classes of stainless steels (martensitic, ferritic, austenitic).

b. Equipment Required.

(1) X-Ray fluorescence unit with lithium fluoride analyzing crystal, scintillation detector, and data control panel capable of fixed time/fixed count operation.

(2) NBS stainless steel standards that bracket the range of the sample.

(3) Sample holders for specimen and standards.

c. Conduct of Test.

(1) Allow the instrument to warm up. Refer to the instruction manual as necessary.

(2) Place the sample and standards in their holders.

(3) Insert the specimens and samples into the X-ray fluorescence unit.

(4) Apply X-rays to the unit. A setting of 35 kv, 20 ma is suggested for a tungsten target.

(5) Determine the attenuation factor by scanning the two-theta angle from 72° to 67° for chromium and 50° to 46° for nickel. Perform this operation with the standards that contain the largest amounts of chromium and nickel.

(6) After determining the proper attenuation setting, scan the standards and samples to determine the two-theta angle of maximum fluorescence. The nickel value should be 48.7° and the chromium value 69.3°. (These values correspond to 1st order KA1,2 excitation.)

(7) Set the data control panel for fixed time/continuous count. A fixed count of 100 seconds is suggested.

5.14.4 Data Required

a. Obtain the total count (pulses) registered in 100 seconds for each specimen and standard.

b. Obtain the total counts per second (CPS) for each specimen and standard.

5.14.5 Data Reduction and Presentation

a. Plot cps versus concentration of chromium on Cartesian coordinate graph paper. This is the working curve.

b. Read the concentration of chromium in the sample(s) from the working curve by drawing a straight line from the cps of the sample(s) to the concentration of chromium.

c. Repeat steps a and b for nickel.

5.15 Determination of Furfural in Furfuryl Alcohol by Infrared Spectroscopy

5.15.1 Objective: To determine the furfural content of furfuryl alcohol. Furfuryl alcohol is manufactured from furfural at elevated pressure and temperature; residual furfural is always present.

5.15.2 Standards: MIL-P-45702B utilizes a bisulfite-iodine titrimetric method to determine the furfural content; this TOP utilizes an infrared (IR) method to determine furfural in the concentration range necessary to satisfy MIL-P-45702B.

5.15.3 Method

a. Scope. This method determines the furfural content of furfuryl alcohol in the range up to 1.0 percent by weight.

b. Equipment Required

(1) IR Spectrophotometer, double beam, covering the fundamental region and operating in linear transmittance versus linear wavenumber

(2) Sealed-demountable IR liquid cell of 0.025-0.040 mm thickness

(3) Analytical balance, ± 0.05 mg sensitivity, 0.1 mg accuracy

(4) Glass syringe, 5 ml

(5) Furfural, 98+ percent purity

(6) Flint glass weighing bottles

(7) Pipets, Class A, 0.1 ml, with 0.01 ml graduation, and 15.0-ml volumetric pipet

c. Preparation of Standards

(1) Pipet 15.0 ml of the furfuryl alcohol sample into three tared weighing bottles

(2) Weigh to the nearest 0.0001 gm.

(3) Add 0.02, 0.04, and 0.08 ml of furfural, respectively, to the weighing bottles.

(4) Mix well, and weigh to the nearest 0.0001 gm.

(5) Calculate the percent by weight furfural added as follows:

$$\% \text{ by Wt Furfural Added} = \frac{\text{Wt of Furfural Added}}{\text{Total Wt of Sample}} \times 100 \qquad (29)$$

d. Conduct of Test

(1) Use a 5-ml glass syringe to transfer the sample to a sealed-demountable IR liquid cell.

(2) Completely fill the IR cell and cap the exit port.

(3) Record the IR spectrum from 5.0 to 6.5 microns (2000-1500 wavenumbers)

(4) Remove the excess sample with the syringe.

(5) Repeat steps 1, 2, 3, and 4 for each standard. Flush sufficient standard through the cell before recording the spectrum.

5.15.4 Data Required

a. IR spectrum scan for sample and standards

b. Absorbance for sample and standards

5.15.5 Data Reduction and Presentation

a. Maximum absorption occurs at about 1680 wavenumbers, due to the carbonyl group on furfural.

b. Draw a straight line joining the absorption minimum on each side of the absorption maximum.

c. Draw a straight line from the absorption maximum to the line joining the absorption minimum. Calculate the absorbance from the

following equation:

$$A = \log_{10} \frac{T_{max}}{T_{min}}$$

where: $\log_{10}$ = log to the base 10

T_{max} = maximum percent transmittance

T_{min} = minimum percent transmittance

d. Determine the absorbance for each standard and sample.

e. Subtract the A of the sample from each standard.

f. Plot the A of the standards versus the concentration of furfural added to each standard. This is the working curve.

g. From the working curve and the absorbance of the sample, obtain the concentration of furfural in the sample.

5.16 Determination of Silicon in a High-Iron Matrix Using X-ray Spectroscopy and Pulse Height Analysis

5.16.1 Objective: To determine the silicon content in steels. The 4th order iron K beta and scattered background radiation interfere with the determination of silicon in steel samples. Pulse height analysis (PHA) allows the determination of silicon in an iron matrix by discriminating against the 4th order iron pulses and producing a concomitant increase in signal-to-noise ratio of the silicon intensity.

5.16.2 Standards: The standards employed in this determination were NBS stainless and tool steel samples, 1-$\frac{1}{4}$ inch in diameter, $\frac{1}{4}$ inch thick, with an iron content from 50.7 to 85.3%. The silicon content of the standards should bracket the suspected sample concentration.

5.16.4 Method

a. Scope. This method may be used to analyze silicon in the range of 0.3 to 1.2% by weight in steel samples, with a relative error of ±16%.

b. Equipment Required

(1) X-ray fluorescent unit with goniometer, pentaerythritol detector, and data control panel capable of PHA and fixed-time/fixed-count operation

(2) P-10 gas (a mixture of 10% methane in argon)

(3) Silicon wafer standard

(4) Vacuum pump, motor driven

(5) NBS stainless steel and tool steel standards

c. Conduct of Test

(1) Energize x-ray control panel.

(2) Place the silicon wafer standard, sample(s), and standards in the specimen holders.

(3) Place all samples and standards in the x-ray fluorescent unit.

(4) Position the silicon wafer to receive the incident x-radiation.

(5) Evacuate the sample chamber and then close the bleeder valve to the sample chamber.

(6) Apply x-rays to the tube target.

(7) Adjust the proportional gas (P-10) to a flow rate of 0.5 cubic feet per minute.

(8) Manually set the goniometer at 109°.

(9) Adjust the high voltage to the detector such that a maximum pulse rate is obtained for the lowest applied voltage; that is, produce a maximum gas amplification without reaching the discharge region.

(10) Scan the region from 106° to 111° and note the angle of peak silicon radiation.

(11) Set the goniometer to the angle determined from step 10 and repeat step 9. Lock the goniometer at this angle.

(12) Conduct a PHA scan on the silicon wafer to obtain a pulse distribution. The PHA scan is obtained by varying the baseline (lower discriminator level) and window (pulse amplitudes greater than the baseline) voltages such that of all pulses reaching the analyzer input, only those pulses due to silicon are registered.

(13) Set the baseline and window voltages obtained in step 12.

(14) Using PHA, scan the samples and standards from 106° to 111°.

(15) Lock the goniometer in place at the angle of peak silicon radiation.

(16) Set the control panel for fixed time/continuous count mode and a fixed time of 200 seconds.

(17) Obtain triplicate readings in counts per second (cps) for each sample/standard.

(18) Repeat steps 16 and 17 with a goniometer setting outside the distribution angle of silicon pulses. This value is obtained from step 14 and constitutes background (noise).

5.16.4 Data Required. Obtain the cps for each specimen and the background cps for each specimen.

5.16.5 Data Reduction and Presentation

a. Subtract the background cps from the silicon cps.

b. Obtain a working curve by plotting on Cartesian coordinate graph paper the cps of silicon versus concentration.

c. Read the concentration of silicon in the unknown from the working curve.

6. DATA REDUCTION AND PRESENTATION. Because of the large number of tests contained in this test operations procedure, the data reduction and presentation section has been incorporated into the individual tests for clarity and ease of handling by the user.

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APPENDIX A. SELECTED BIBLIOGRAPHY

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HYDROGEN PEROXIDE DETERMINATION, WORKSHEET

DATE _____ INITIALS _____

1) CAS Equivalence Ratio R = NB

CAS (A) (ml)			
$FeSO_4$ (B) (ml)			
R			
Mean			

2) Normality of CAS

Normality of $K_2Cr_2O_7$ (C)_____ $N = \frac{C \times D}{E \times R - F}$

$K_2Cr_2O_7$ (D) (ml)			
$FeSO_4$ (E) (ml)			
CAS (F) (ml)			
N			
Mean			

3) $\% H_2O_2 = \frac{(G - H \times R) K \times 100}{W \times L/M}$ $K = 0.01701$ gm/meq $\times N =$ _____

Sample Number						
Wt Flask + Sample (gm)						
Wt Flask + Sample (gm)						
Wt Sample (W) (gm)						
Volume H_2O_2 Aliquot (L) (ml)						
CAS (G) (ml)						
$FeSO_4$ (H) (ml)						
$\% H_2O_2$						
Mean						

TIN IN HYDROGEN PEROXIDE DETERMINATION, WORKSHEET

DATE_____INITIALS_____

Sample Number			
Volume Original Sample (V_1) (ML)			
Volume Concentrated Sample (V_2) (ML)			
Volume Aliquot (V_3) (ML)			
Standard Sn Solution Added			
Volume Test Solution (V_4) (ML)			
Absorption			
Zero Absorbance Intercept (I) $\frac{\mu g}{ml}$ Sn			
Hydrometer Reading			
Hydrometer Correction			
Corrected Hydrometer Reading (D)			

$$C = \frac{I \times \frac{V_4}{V_3} \times V_2}{V_1 \times D}$$

C = ppm Sn

HCl IN AIR DETERMINATION, WORKSHEET

DATE_____ INITIALS_____

Sample Number								
Barometric Pressure (mm Hg)								
Manometer Pressure (mm Hg)								
P(INT) (mm Hg)								
Volume $AgNO_3$ (A) (ml)								
Volume Sample Bottle (V_s) l								
Room Temperature (°C + 273) (T_r) °K								
ppm HCl								

$$N(AgNO_3) = \frac{\text{ml KCl} \times [N(KCl)]}{\text{ml } AgNO_3}$$

$$\text{ppm HCl} = \frac{A \cdot N(AgNO_3) \times 22.4 \times 10^{6} \frac{\text{ml}}{\text{mol}} \cdot \frac{1 \text{ mol HCl}}{10^{3} \text{ meq HCl}}}{V_s \left(\frac{P(INT)}{760 \text{ mm Hg}}\right)\left(\frac{273° K}{Tr° K}\right)}$$

ml KCl _____

N(KCl) _____

Ml $AgNO_3$ _____

N($AgNO_3$) _____

DETERMINATION OF DIOCTAL ADIPATE IN SOLID PROPELLANT, WORKSHEET

Sample Number_____ DATE_____ INITIALS_____

(1) Synthetic propellant:

Tare 1 + DOA		gm	
Tare 1	_____	gm	
DOA		gm	____%
Tare 1 + DOA + NH_4ClO_4		gm	
Tare 1 + DOA	_____	gm	
NH_4ClO_4		gm	____%
Tare 1 + DOA + NH_4ClO_4 + KBr		gm	
Tare 1 + DOA + NH_4ClO_4	_____	gm	
KBr		gm	____%

(2) Reference propellant mixture:

Tare 2 + synthetic propellant		gm
Tare 2	_____	gm
Synthetic propellant		gm
Tare 2 + synthetic propellant + KBr + NaN_3		gm
Tare 2	_____	gm
Reference propellant mixture		gm

(3) Weight percent DOA in reference propellant mixture:

$$\text{Wt \% DOA} = \frac{\text{Wt Synthetic Propellant (gm)} \times \text{Ratio DOA in Synthetic Propellant} \times 100}{\text{Wt Ref Propellant Mixture (gm)}}$$

Wt % DOA =

(4) Propellant mixture:

Tare 3 + propellant		gm
Tare 3	_____	gm
Propellant		gm

Tare 3 + propellant + $KBr + NaN_3$ _____ gm

Tare 3 _____ gm

Propellant + $KBr + NaN_3$ _____ gm

(5) Absorption data:

$$A(DOA)/A(NaN_3)$$

Propellant mixture pellet _____

Reference propellant mixture pellet _____

(6) Weight percent DOA in propellant mixture:

$$\frac{\text{Ratio DOA in Ref Propellant}}{\text{Absorbance Ref Propellant Mixture}} = \frac{\text{Wt \% DOA in Propellant Mixture}}{\text{Absorbance Propellant Mixture}}$$

Wt % of DOA in Propellant Mixture = _____

(7) Weight percent DOA in propellant:

$$\text{Wt \% DOA in Propellant} = \frac{\text{Ratio DOA in Propellant Mixture} \times \text{Weight Propellant Mixture} \times 100}{\text{Wt Propellant}}$$

Wt % DOA in Propellant =

ALLOYING ELEMENTS IN STEEL DETERMINATION, WORKSHEET

DATE_____ INITIALS_____

Sample Number	Element	Element Line	T_r(E)	S(E)	Internal Standard Line (Fe)	T_r(Fe)	S(Fe)	S(E) - S(Fe)	%(E)

CARBON DIOXIDE AND CARBON MONOXIDE IN AIR DETERMINATION, WORKSHEET

DATE _____ INITIALS _____

Barometric Pressure _____ mm Hg

Sample Number	Cell Pressure (mm Hg)	CO_2					CO				
		I_b	I_s	(I_b/I_s)	Log (I_b/I_s)	ppm	I_b	I_s	I_b/I_s	Log (I_b/I_s)	ppm

HYDROCARBONS IN COMPRESSED AIR DETERMINATION, WORKSHEET

DATE _____ INITIALS _____

Volume of Multiple Pathlength Cell

$$V_c = V_a\left(\frac{P_a}{P_c} - 1\right)$$

V_a = _____ l

P_a = _____ mm Hg

P_c = _____ m Hg

V_c = _____ l

Original Sample Volume = Flowrate x time
l/min x min = l

Barometric Pressure _____ mm Hg

Sample Number	Sample Volume (l)	Cell Pressure (mm Hg)	Hydrocarbons				
			I_b	I_s	I_b/I_s	Log (I_b/I_s)	ppm

FLUORIDE IN WATER DETERMINATION, WORKSHEET

DATE_____INITIALS_____

Sample Number	Voltage (mV)	Original Volume (ml)	Buffered Sample (ml)	ppm F^-

DETERMINATION OF OXYGEN BY NAA, WORKSHEET

DATE_____INITIALS_____

	Standard	Comparison Standard	Sample
Wt Container +	gm	gm	gm
Wt Container	gm	gm	gm
Weight	(W_s) gm	(W_c) gm	(W) gm

Standard_____Oxygen_____% Diameter Sample_____cm Volume Sample_____cm

Number of Counts for Standard C_s_____cts

Number of Counts for Sample C_u_____cts

Time of Irradiation_____

Time of Background Count_____

$$R_c = \frac{C_u}{C_s} = \frac{\text{cts}}{\text{cts}} = \text{_____}$$

$$R_e = \frac{W_c}{W_s \times R_c} = \text{_____}$$

Correction for Self-absorption

$$SA = \exp(-\bar{\mu}l\frac{W}{V}d) \simeq 1 - \bar{\mu}l\frac{W}{V}d, \quad d = 0.550$$

$(SA)_s$ = _____

$(SA)_u$ = _____

$$(SA)_{corr} = \frac{(SA)_s}{(SA)_u} = \text{_____}$$

$$\Sigma_T = \frac{1}{V}\sum_i^{\sigma_T}(14\ \text{Mev})_i \frac{Wi}{Mi} \times NA$$

Σ_T = _____

$SS = D \times \Sigma_T$

$(SS)_s$ = _____

$(SS)_u$ = _____

$$SS_{corr} = 1 + \left[(SS)_u - (SS)_s \times F_{ss}\right]$$

(For F_{ss} use .023)

$$O_x = R_c \times R_e \times \frac{W_{os}}{W_u}\ (SS_{corr}) \times SA_{corr} \times 100$$

O_x = _____%

NITROBENZENE IN ANILINE DETERMINATION, WORKSHEET

SAMPLE NUMBER_____ DATE_____ INITIALS _____

Wt Bottle + AN + NB					
Wt Bottle + AN					
Wt Bottle					
Wt AN + NB					
Wt NB					
% NBA = $\frac{\text{WT NB}}{\text{WT AN + NB}} \times 100$					
h					
CS					
id = C_s x h					

$$\frac{\%\ \text{NBA} + X}{ids} = \frac{X}{idx}$$

X				

COPPER IN WATER BY AAS DETERMINATION, WORKSHEET

DATE _____ INITIALS _____

Sample Number	Volume (ml)	Absorbance	Concentration

DETERMINATION OF TEA IN FURFURYL ALCOHOL BY GC, WORKSHEET

SAMPLE NUMBER_____ DATE_____ INITIALS_____

Wt Bottle + FA + TEA				
Wt Bottle + FA				
Wt Bottle				
Wt FA + TEA				
Wt TEA				
% TEA (added) = $\frac{\text{wt TEA}}{\text{wt FA + TEA}}$				
Peak Height (PHT)				
PHT - PHT Sample				

% TEA _____

DETERMINATION OF CHROMIUM AND NICKEL IN STAINLESS STEEL BY XRS, WORKSHEET

DATE _____ INITIALS _____

Sample Number	Chromium			Nickel		
	counts/100's	cps	% Cr	counts/100's	cps	% Ni

DETERMINATION OF FURFURAL IN FURFURYL ALCOHOL BY IR, WORKSHEET

SAMPLE NUMBER_____ DATE_____ INITIALS_____

Wt Bottle + FA + Furfural				
Wt Bottle + FA				
Wt Bottle				
Wt FA + Furfural				
Wt Furfural				
% Furfural Added = $\frac{\text{wt Furfural x 100}}{\text{wt FA + Furfural}}$				
T_{max}				
T_{min}				
A				
A - A Sample				

% Furfural _____

DETERMINATION OF SILICON IN A HIGH-IRON MATRIX USING XRS AND PHA, WORKSHEET

DATE_____ INITIALS_____

Sample Number	Si		Background		$cps_{(Si)} - cps_{(BG)}$	% Si
	counts/200's	cps	counts/200's	cps		

SUPPLEMENTARY

INFORMATION

SECURITY CLASSIFICATION OF THIS PAGE *(When Data Entered)*

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REPORT DOCUMENTATION PAGE

READ INSTRUCTIONS BEFORE COMPLETING FORM

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Chemical agents
Organic vapors

20. ABSTRACT *(Continue on reverse side if necessary and identify by block number)*

This TOP prescribes a method for the evaluation of missile system materials and identifies chemical analyses, facilities, and equipment for use, as appropriate. It provides procedures for propellant, gas, and metal tests. Applicable to missile system material properties determinable by chemical tests.

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SECURITY CLASSIFICATION OF THIS PAGE *(When Data Entered)*

US ARMY TEST AND EVALUATION COMMAND

Aberdeen Proving Ground, Maryland 21005-5055

TOP 5-2-585
AD A047970
Change 2

20 September 1985

CHEMICAL TESTS: PROPELLANTS, GASES, AND METALS

TOP 5-2-585, 11 December 1975, is changed as follows:

1. Remove pages and insert new pages as indicated below:

Remove pages	Insert pages
1/2	1/2
91/92	91/92
A-1/A-2	A-1/A-2

2. Add pages 93 through 96.

3. A vertical line in the left margin indicates the changed portions of the revised pages.

4. Attach this sheet to the front of the reference copy for information.

US ARMY TEST AND EVALUATION COMMAND
TEST OPERATIONS PROCEDURE

AMSTE-RP-702-104 20 September 1985
*Test Operations Procedure 5-2-585, C2
AD No. A047970

CHEMICAL TESTS: PROPELLANTS, GASES, AND METALS

The use of trade names in this test operations procedure does not constitute an official endorsement or approval of the use of such commercial hardware or software. This test operations procedure may not be cited for purposes of advertisement.

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*This TOP supersedes TOP 5-2-585, 15 February 1972

c. Preparation for test

(1) Ionic Strength Adjustor (ISA). Prepare 5M $NaNO_3$ by dissolving 42.5g of reagent grade $NaNO_3$ in 100 ml distilled water.

(2) Prepare a series of standards with a 1000 ppm Cl^- stock solution. The stock solution is prepared by weighing out 0.2103g KCl and diluting to the mark in a 100 ml volumetric flask with distilled water. Then prepare a 10 ppm Cl^- solution by diluting 1 ml of 1000 ppm Cl^- to 100 ml. Prepare standards of 2 ppm, 1 ppm, 0.5 ppm, 0.2 ppm, 0.1 ppm, and 0 ppm (blank) Cl^- by dilution, each standard containing 2 ml of ISA and having a total volume of 100 ml. Standards should be made fresh before each use.

(3) Prepare a rinse solution by diluting 20 ml of ISA to IL with distilled water. This solution should also be used as the reference portion of the H-cell.

(4) Prepare the scrubber by cleaning thoroughly, then adding 100 ml distilled water. After sampling, the solution should be placed in a 100 ml volumetric flask, 2 ml ISA added, and the flask filled to the mark with distilled water. It is also advisable to run a background sample. Be sure that the scrubber and pump assembly are well protected from damage or shock during the firing.

(5) Prepare the H-cell by rinsing with double distilled water. Add 1g of agar to 25 ml of the ISA rinse solution and heat to near boiling. Fill a 5 ml syringe with the fluid solution. Fix the H-cell in a horizontal position, and using the syringe, fill the cross-bar with the agar solution. Cool completely in this position before using.

d. Determination of HCl. Use the rinse solution (ISA) in the reference side of the H-cell, and use the ISA solution to rinse the sample portion of the cell in between each standard or sample. Measure each standard by the single negative ion mode on the specific ion meter. Run the field samples and background sample and record the readings. If the readings drift or take a long time to stabilize, polish the bottom of the Cl^- electrode with a polishing strip.

5.18.4 Data Required

a. Concentration of standards

b. Readings from specific ion meter of standards and samples

c. Flow rate of limiting orifice

d. Sampling time

5.18.5 Analytical Plan

a. Plot a calibration curve of concentration versus meter reading for each standard. Determine the concentration of the field and background

samples from the curve. If the background is negligible, use the value obtained from the field sample as the result. Otherwise, subtract the background from the field sample to obtain the final value in ppm. The curve will level off (and become nonlinear) at very low concentrations of Cl^-.

b. Convert ppm to mg/M^3. For a flow rate of 10 L/min, sampling time of 2 minutes,* and sample volume of 100 ml,

$$mg/M^3\ HCl = \frac{ppm\ Cl^- \times \frac{36.46}{35.45} \times 1000\ L/M^3 \times 0.1\ L}{2\ min \times 10\ L/min}$$

$$mg/M^3\ HCl = ppm\ Cl^- \times 5.142$$

5.19 Determination of Offgassed Organic Vapors in Air

5.19.1 Objective: To identify and quantify the organic vapors that offgas from the paints/primers used in military materiel (References 19, 20, 21).

5.19.2 Standards:

Compound	Desorption Efficiency (percent)	Sampling Rate (cc/min)	Time Weighted Average (TWA) ppm
m-Xylene	95 ± 5	200	100
o-Xylene	95 ± 5	200	100
p-Xylene	95 ± 5	200	100
Toluene	92 ± 5	200	200
2-Butanone	85 ± 5	200	200
4-Methy-2-Pentanone	85 ± 5	200	100
Ethyl Benzene	100	200	100
Cyclohexane	100	200	300
1-Butanol	88 ± 5	200	100
n-Butyl Acetate	99 ± 5	200	150
Benzene	96	200	1

5.19.3 Method

a. Scope: This method involves the use of charcoal tubes to collect solvent vapors in series with a portable personal pump followed by desorption and analysis by gas chromatography. Some components of paint are toxic and/or carcinogenic (Ref 23).

*This time is representative of the duration of an exhaust gas cloud.

b. Limitations:

(1) Solvents may be displaced by other solvents that are more strongly adsorbed by the charcoal.

(2) There is a saturation limit for each solvent and when this limit is exceeded, the solvent is no longer adsorbed by the charcoal. This is called "breakthrough."

(3) High humidity decreases the adsorption efficiency of the charcoal.

c. Equipment and reagents required:

(1) Laboratory fume hood.

(2) Glass charcoal tubes, ends sealed, 7 cm long, with a 6-mm outside diameter and 4-mm inside diameter, containing two sections of 20/40 mesh activated charcoal separated by a 2-mm portion of urethane foam. The front section contains 100 mg charcoal; the backup end contains 50 mg of charcoal. (Ref 24)

(3) Calibrated, battery-operated personal sampling pumps capable of sampling at rates from 0.1 to 1.0 L/min. (Ref 24)

(4) ACS-grade carbon disulfide.

(5) ACS-grade reagents of the compounds under investigation.

(6) Glass-stoppered microtubes.

(7) Gas chromatograph (GC) with a flame ionization detector, an area integrator system, and programmable oven temperature.

(8) 10-μL syringes.

(9) 10-mL volumetric flasks.

(10) A 6-foot GC column of 10% carbowax 20 mesh terephthalic acid derivative (Free Fatty Acid Phase) on 80/100 mesh chromasorb W that is AW-DMCS treated.

(11) 1.0-mL pipettes graduated in 0.1-mL increments.

(12) 10.0-mL TD volumetric pipettes.

(13) Filtered compressed air.

(14) Grade A helium.

(15) Ultra-high-purity hydrogen (purity of 99.999 mole%).

(16) Refrigerator.

5.19.4 Procedures:

a. Detergent wash and thoroughly rinse all glassware with tap water followed by distilled water.

b. Snap the ends of the charcoal tubes and insert the smaller charcoal end (50 mg) nearest the personal pump. The charcoal tube should be vertical to prevent channeling of the charcoal.

c. Calibrate the flow rate of each personal pump with a charcoal tube in place. Perform a system leak test; no leakage should be observed.

d. Remove the charcoal tube used in paragraph c and discard. Prepare the personal pumps for sampling as in paragraph b.

e. Place the personal pumps in the areas to be sampled.

f. At the sampling area, open one charcoal tube and cap the charcoal tube with the caps provided. Never use rubber caps. No air is drawn through this tube, which serves as a blank. (Ref 24)

g. Energize the personal pumps and collect a sample volume of 3-6 liters.

h. Accurately measure the flow rate, duration of sample collection, ambient temperature and barometric pressure.

i. At the conclusion of the sampling interval, cap the charcoal tubes with the caps provided. Never use rubber caps. (Ref 24)

j. Label each charcoal tube, transfer to the laboratory, and refrigerate overnight.

k. For each compound under investigation, remove the 100 mg charcoal portions from five unused charcoal tubes and place in separate microtubes.

l. Inject the TWA (time weighted average) - OSHA concentration, for each compound under investigation, onto the charcoal, seal, and allow to stand overnight. (Ref 24)

m. Set aside a 100 mg charcoal section as a blank in a microtube. Seal and allow to stand overnight.

n. The following day, remove the refrigerated samples and transfer each section of charcoal into separate microtubes. Seal and label each microtube.

o. Prepare calibration standards, in 10.0 mL volumetric flasks, by adding 10.0 mL of carbon disulfide to produce standards equivalent to 0.5, 1.0, 2.0, and 5.0 µL/mL for each compound analyzed.

p. In a hood, desorb all samples, blanks, and TWA-OSHA standards by adding 1.0 mL of carbon disulfide to each microtube. Seal and shake occasionally for 1 hour.

q. Using a glass stoppered microtube, prepare efficiency standards by injecting the TWA-OSHA volume into 1.0 mL of carbon disulfide for each compound analyzed.

r. Set the following operating parameters for the GC:

Helium Flow Rate	30 cc/min
Hydrogen Flow Rate	30 cc/min
Air Flow Rate	400-450 cc/min
Oven Temp Initial Value	75°C
Oven Temp Initial Time	5.0 min
Oven Temp Program Rate	5.0°C/min
Oven Temp Final Value	150°C
Oven Temp Initial Time	15.0 min
Detector Temperature	220°C
Injector Temperature	200°C
Chart Speed	1.0 cm/min
Attenuation	2^9
% Offset	10
Threshold	4
Peak Width	0.04

These parameters were used with a Hewlett-Packard 5880 GC; the parameters may be varied to optimize results.

s. Using the "solvent flush technique," inject 5 µL from each 100 mg charcoal sample into the GC. Run in triplicate. (Ref 24)

t. Repeat paragraph s for each backup section (50 mg charcoal). If the concentration is greater than 10% of the front section, suspect breakthrough.

u. Repeat paragraph s for the calibration standards and desorption efficiency samples.

5.19.5 Data Required

a. Temperature at which the samples were obtained.

b. Barometric pressure at which the samples were obtained.

c. Sampling time.

d. Flow rate.

e. The integrated areas for samples, blanks, and standards.

f. The volume of air sampled.

g. The retention times of the standards and samples.

h. The molecular weight and density of each compound analyzed.

5.19.6 Data Reduction and Presentation

a. Subtract the appropriate blank areas from the samples, calibration standards, and efficiency standards.

b. Plot solvent concentration (µL/mL) versus peak integrated areas for each calibration standard to obtain the calibration curve for each compound.

c. Determine the µL of solvent desorbed from the calibration curve for each compound.

d. Determine the ppm of solvent from the following equation:

$$ppm = \frac{(\mu L \text{ solvent})(24450)(D)}{(MW)(Vs)}$$

where: Vs = Volume of air sampled (liters) corrected to 25°C and 1 atm
D = density of compound (g/cc)
MW = molecular weight (g/mole)
24450 = Molar Volume (cc/mole) at 25°C and 1 atm

e. Determine the desorption efficiency for each compound from the following equation:

$$\% \text{ efficiency} = \frac{\text{area of sample X 100}}{\text{area of efficiency standard}}$$

f. Average the desorption efficiencies.

g. Determine the ppm for each compound by adding the ppm obtained from each charcoal section.

h. Determine the true ppm for each compound by multiplying the total ppm by 100 and dividing by the desorption efficiency.

6. DATA REDUCTION AND PRESENTATION. Because of the large number of tests contained in this test operations procedure, the data reduction and presentation section has been incorporated into the individual tests for clarity and ease of handling by the user.

Recommended changes to this publication should be forwarded to Commander, U.S. Army Test and Evaluation Command, ATTN: AMSTE-TC-M, Aberdeen Proving Ground, Maryland 21005-5055. Technical information may be obtained from the preparing activity: Commander, U.S. Army White Sands Missile Range, ATTN: STEWS-TE-P, White Sands Missile Range, New Mexico 88002-5031. Additional copies are available from the Defense Technical Information Center, Cameron Station, Alexandria, Virginia 22304-6145. This document is identified by the accession number (AD No.) printed on the first page.

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